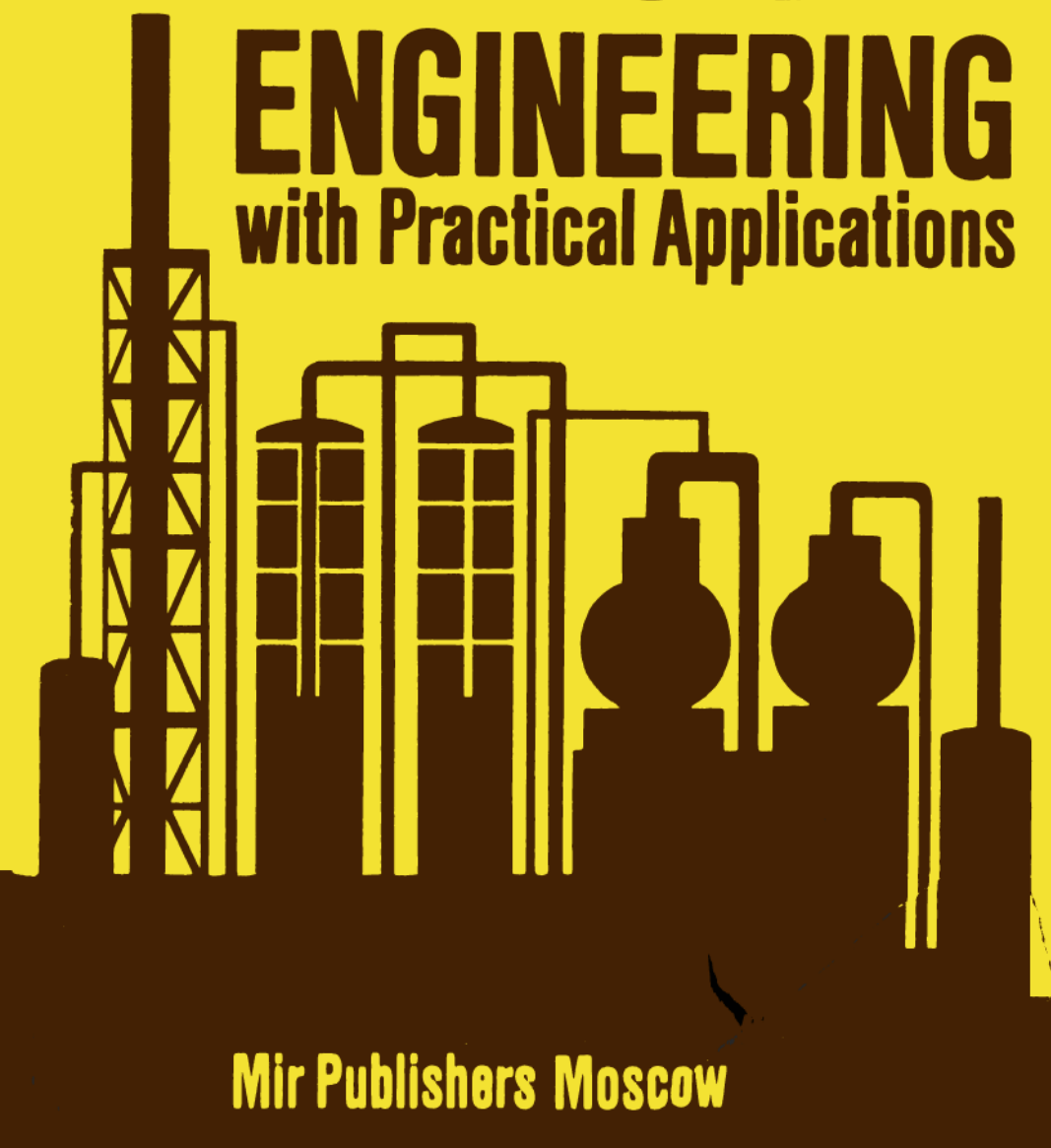


A.M.Kutepov, T.I.Bondareva, M.G.Berengarten

BASIC CHEMICAL ENGINEERING

with Practical Applications



Mir Publishers Moscow

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 and Hydrogen Based Syntheses
An Outline of Bioengineering

A.M.Kutepov, T.I.Bondareva, M.G.Berengarten

BASIC CHEMICAL ENGINEERING **with Practical Applications**

This is a text tailored to the needs of chemical-engineering college students. Its material encompasses a broad gamut of matters. Notably, it includes a discussion of thermodynamics and chemical kinetics, reactor classification and design, the principles underlying chemical-processes, and quite a number of examples illustrating their application in the chemical-process industry.



А.М. Кутепов, Т.И. Бондарева, М.Г. Беренгартен

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A.M.Kutepov, T.I.Bondareva, M.G.Berengarten

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INTRODUCTION

1.1 Chemical Engineering Defined

In a wider sense, *engineering* may be defined as a scientific presentation of the techniques and facilities used in a particular industry. For example, mechanical engineering refers to the techniques and facilities employed to make machines. It is predominantly based on mechanical forces which are used to change the appearance and/or physical properties of the materials being worked, while their chemical properties are left unchanged. Chemical engineering encompasses the chemical processing of raw materials, based on chemical and physico-chemical phenomena of high complexity.

✓ Thus, **chemical engineering is that branch of engineering which is concerned with the production of bulk materials from basic raw materials in a most economical way by chemical means.**

(It seems relevant to recall what Dmitry I. Mendeleev of Russia once wrote on the difference between chemical and mechanical engineering: "...Beginning with an imitation, any mechanical manufacturing may perfect itself even in its underlying principles, provided there is enough motivation and capacity to observe. With this alone, however, but without advance knowledge, the progress of chemical processing is hardly conceivable — it is non-existent and will, in all appearance, never exist... . This is because all chemical transformations... are hidden, occur at the molecular level, do not reveal their mechanism, and their conscious control call for a knowledge comparable with that of mechanical changes. Otherwise the doer will simply be unable to see the mechanisms essential to chemical processing.")

Drawing upon advances in the natural and technical sciences, chemical engineering today is investigating and developing a wide gamut of physical and chemical processes, machines and apparatus, and also optimal pathways for the realization and control of these processes and plant in the industrial production of substances, materials, products, and goods.

(Chemical engineering is above all based on the chemical sciences, such as physical chemistry, chemical thermodynamics, and chemical kinetics.) In doing so, however, it does not simply copy their findings, but adapts them to bulk chemical processing. In the words of Academician Konovalov, one of the principal objectives that set chemical engineering apart from chemistry as a pure science, is "to find the most economical route of opera-

tion and to design commercial equipment and accessories that suit it best of all". Therefore, chemical engineering is inconceivable without close ties with economics, physics, mathematics, cybernetics, applied mechanics, and other technical sciences.

In its early days, chemical engineering was largely a descriptive science. Many of the early textbooks and manuals on chemical engineering were encyclopedias of the commercial production processes known at the time. Progress in science and industry has brought with it an impressive increase in the number of chemical manufactures. Today, petroleum for example serves as the source material for the production of about 80 thousand chemicals. The expansion of the chemical process industries on the one hand and advances in the chemical and technical sciences on the other have made it possible to lay theoretical foundations for chemical processing.

As the chemical process industries forged ahead, new data, new relationships and new generalizations were added to the subject-matter of chemical engineering. Many branches in their own right have separated from the main stream of chemical engineering, such as process and plant design, automation, chemical process simulation and modelling, etc.

In recent years, chemical engineering has received big impetus owing to the use of computers in handling both theoretical and applied problems. Apart from being powerful tools in achieving ever more complex tasks, computers have enriched chemical engineering with novel approaches based on mathematical modelling and systems research. There has been a steady progress in an entirely new division of chemical engineering — the cybernetics of chemical processing.

Advances in chemical engineering as a science are inseparable from its commercial applications. In recent decades the chemical process industries have taken a firm position among the leading divisions of material production. New discoveries and processes are commercialized in a progressively shorter time and provide close ties between science and industry. These ties have proved extremely valuable in the judicious use of raw materials, fuel, and energy, in the development of novel wasteless processes in which the reactions involved proceed at high rates, under optimal conditions, and yield high-quality end products.

1.2 A Brief Historical Outline

Historically, chemical engineering is inseparable from the chemical process industries. In its early days chemical engineering which came into being with the advent of early chemical trades was a purely descriptive division of applied chemistry.

The manufacture of basic chemical products in Europe appears to have begun in the 15th century when small, specialized businesses were first set

up to turn out acids, alkalis, salts, pharmaceutical preparations, and some organic compounds. In Russia, the origin of what might be called a chemical industry dates back to the late 16th — the early 17th century, and included the manufacture of dyes, saltpetre, gun powder, soda, and sulphuric acid.

In the later half of the 18th century, chemical engineering began to acquire the status of an independent division of knowledge as the foundation was being laid for it as a science and a subject of instruction. For the first time it was called as what might come across as chemical engineering in 1772 by J. Beckman, Professor of the Göttingen University, who was also the first to publish comprehensive works on many chemical manufactures. In fact, they made up the ever first textbook on chemical engineering. In 1795, Gmelin of Germany turned out a two-volume course in “technical chemistry”.

In 1803, the Russian Academy of Sciences set up the Chair of Chemical Engineering. In 1804, the first Russian periodical, “The Chemical Engineering Journal, or a Collection of Works on Chemical Engineering”, first appeared in St. Petersburg, Russia. At about the same time, chemical engineering was included in the curricula of the Russian institutions of higher learning.

Ivan A. Dvigubsky, Professor of Moscow University, the author of the first Russian textbook on chemical engineering, which was published in 1807–1808 under the title “The Basic Foundations of Chemical Engineering or a Brief Exposition of Processing Done at Factories”, wrote in the preface to the book: “Nowadays, nearly all well-organized colleges offer a course in engineering, or the science of crafts and factories, so that those who have devoted their lives to sciences could overview the entire domain of engineering and promote, through their theoretical knowledge, the further dissemination and perfection of crafts and factories essential to the growth of public wealth”.

In the 19th century, quite a number of textbooks, manuals and studies in chemical engineering were published in Western Europe and Russia. Their appearance was fostered by the rapid expansion of chemical processing and, along with it, advances in the scientific foundations of chemical engineering. Owing to the limited scope of this book, only some of the highlights in this field can be mentioned.

In 1748, the first small factory was built in Birmingham, England, to make sulphuric acid in lead chambers (this was the early form of the chamber process). The large-scale use of this process dates back to 1805–1810 in England and France, to 1805 in Russia, and to 1820 in Germany.

In 1787–1789, Nicolas LeBlanc of France developed the first commercial process for the manufacture of soda. His invention was in great de-

mand because large quantities of this product were needed in the manufacture of glass, caustic soda, and other products. (The first large soda factory using the LeBlanc process was built in England in 1823.) In 1861, Ernest Solvay, a chemist-industrialist, came out with an alternative process for the manufacture of soda ash from salt by the agency of ammonia (the Solvay process, sometimes designated as the ammonia-soda process).

The latter half of the 19th century saw an ever growing scientific interest in catalysis, owing to which many new chemical manufacturing processes could be commercialized. One example is the discovery of the contact process for the manufacture of sulphuric acid in the 1870s. In 1886, this process was commercialized.

A new period in the history of organic chemistry was marked by the integration of heterogeneous catalysis in organic syntheses. Early in the 19th century, prominence was gained by syntheses on the basis of hydrocarbons and carbon monoxide. Discoveries in the field of heterogeneous catalysis enabled S.V. Lebedev of Russia to come up with his process for the manufacture of synthetic rubber on a commercial basis.

Theoretical and experimental work in chemical thermodynamics was decisive in tackling many of the topical tasks in the chemical process industries. Quite a number of studies in this field had a direct bearing on chemical engineering. Among them, special mention should be made of the work done by Le Chatelier, Nernst and Haber in the synthesis of ammonia from nitrogen and hydrogen. The commercial plant to synthesize ammonia under pressure, built in 1912, came as a veritable breakthrough in the chemical process industries and opened the use of high pressure for chemical processing.

In the mid-19th century, a large-scale follow-up of Justus von Liebig's studies in the field of agricultural chemistry gave rise to a new branch of the chemical process industries — fertilizer manufacture. Without fertilizers, it would be hardly possible to feed the ever-growing population of our planet Earth today.

Theoretical studies carried out in the field of chain reactions in the 30s through 50s of this century had as their technological spin-back several syntheses involving high-pressure polyethylene, polystyrene, PVC, and some other products. The advent of plastic materials, synthetic resins and man-made fibre ushered in a new era in the manufacture of materials having controlled properties.

Studies in chemical engineering that are being carried today in both theoretical and experimental fields also contribute to the development of new materials having controlled properties, intensive farming, environmental control, and many other tasks.

1.3 Basic Trends in State-of-the-Art Chemical Engineering

Basic trends in chemical engineering today are directly related to the global problems facing mankind. These above all are the expansion of the Earth's food supplies, the search for new sources of raw materials for industry, the acquisition of novel energy sources, and the control of the pollution of the biosphere.

All of these problems are interrelated and call for a unified approach to their solution. A major component of this approach is bioengineering. Biological control of toxic substances, the pollution of soil, water and the atmosphere, the microbiological extraction of minerals, biological methods for the production of enzymes and biologically active substances outperform the potentialities of traditional methods in terms of efficiency.

The production of foodstuffs can best be expanded and the reserves of food supplies can be enhanced through the wider use of chemicals for crops and livestock.

State-of-the-art chemical engineering, notably bioengineering, is capable of deriving on a commercial scale and from nonfood raw materials quite a number of foodstuffs, among them monosaccharides, ethanol, glycerol, furfural, yeasts, amino acids, protein-vitamin concentrates, and other products.

One of the objectives of chemical engineering is to derive foodstuffs from mineral materials whose reserves are practically inexhaustable. This will make man more independent of the sudden fluctuations that happen in some years in the production of food biologically.

In order to meet the needs of the chemical process industries in raw materials, work is under way to expand the availability of hydrocarbon feedstock and petrochemical semi-products by deriving more fractions from crude oil, by widely using the gas condensate, through the recovery of all the values present in the hydrocarbons of natural and casing-head gases, with more reliance on non-petroleum raw materials, such as carbon monoxide and dioxide, and on the basis of a better utilization of hydrocarbon raw materials by way of highly selective and utility-saving manufacturing and processing methods.

The supply of raw materials for fertilizer manufacture will be expanded through the better beneficiation of potassium and lean phosphate rock and through the use of secondary materials, such as sulphur-bearing gases from non-ferrous metallurgy and oil refineries, for the manufacture of sulphuric acid.

One of the prevailing trends in chemical engineering, notably in the chemistry of hydrocarbons and the chemical processing of coal and shales, is towards the tonnage production of novel chemicals and source materials

each of which could serve a wide gamut of end uses. Among them are molecular hydrogen, ammonia, hydrazine and methanol — they can double as chemical reactants and alternative fuels.

The most promising uses for hydrogen are the synthesis of ammonia and methanol, the synthesis of liquid and gaseous hydrocarbons (synthetic liquid fuel, methane), the gasification of solid fuels, the direct reduction of metal ores, the sintering of powdered metals, the manufacture of propellants for aerospace applications, fuels for automobiles and gas turbines, and working fluids for MHD generators.

Using inexpensive hydrogen, the carbon dioxide of carbonate rock whose reserves in Nature are truly inexhaustible can readily be converted by hydrogenation into methanol, methane, carbon monoxide, liquid hydrocarbons, and urea.

At this writing, large-scale work is under way in all developed countries of the world, whose objective is to devise economical processes for the tonnage production of hydrogen and to consolidate it into a comprehensive hydrogen technology.

The switch-over to hydrogen will tie together power generation, the chemical process industries, domestic gas supply, metallurgy, the production of automotive and aerospace fuel and propellants, and the manufacture of synthetic hydrocarbons into a single technological entity. The reserves of hydrogen are unlimited and replenishable. Hydrogen technology will do away with all ecological problems and handicaps in the supply of raw materials.

Another important trend is an increased emphasis on nuclear power and heat generation which will in the long run make the huge amounts of fossil materials now burned as fuels, available for use as chemical reactants.

No less important is the fact that the heat of nuclear reactors can be utilized for endothermic high-temperature chemical reactions, and their gamma-radiation for the synthesis and modification of materials by the techniques of irradiation chemistry. The integration of chemical engineering and nuclear power generation will give impetus to further progress in science and technology.

Since the reserves of petroleum in the world are limited, coal takes on an important role as a source of novel starting materials for the manufacture of chemicals and petrochemicals.

In terms of its effect on the environments, man's economic activity has become comparable with natural phenomena and has led in many instances to irreversible and detrimental changes in the biosphere. This is the reason why an ever greater importance is attached to a more enlightened and intelligent use of the biosphere and its protection against harmful technogenic processes. Here chemical engineering can do much by evolving

better ways and means of industrial waste disposal and waste control. The ultimate goal is to devise manufacturing processes that would leave no wastes at all so that nothing would have to be discharged into the atmosphere or into water bodies.

One of the tasks facing chemical engineering, at least in the Soviet Union, is to speed up and expand the commercial production of polymers for use as materials of construction (among them polycarbonates, polyamide, PTFE, polyphenyleneoxide, and others) and also a new generation of polymers possessing better service properties, to use large production units for the purpose and to find ever new applications for them in mechanical engineering, electronics, medicine, civil engineering, fibre optics, and membrane technology. It is important to make wider use of membrane processes in various industries for the separation of liquids and gases, the preparation of very pure substances, photographic materials, chlorine, caustic soda, ammonia, and chemical additives, and also for the treatment of waste waters and the recovery of valuable components from them.

Part One

BASIC CONCEPTS OF CHEMICAL ENGINEERING

THERMODYNAMICS AND KINETICS

Chapter One

THE CHEMICAL PROCESS

A chemical process is an assemblage of individual steps or operations which, when completed, produce a desired end product from a few basic raw materials. Some of the component operations are needed in order to prepare the reactants for a chemical reaction, that is, to make them most reactive. For example, the rate of chemical reactions strongly depends on temperature. This is the reason why the reactants are often heated so that a reaction could proceed properly. To avoid side reactions or in order to obtain a high-quality end product, the feed (that is, the materials originally used for a reaction) may be cleaned of impurities by methods which are based on differences in physical properties between substances (such as solubility in various solvents, density, the temperature of condensation or solidification, etc.). The cleaning of raw materials and feeds widely uses the phenomena that involve heat and mass transfer, and fluid-mechanic processes. The cleaning may also be done chemically, that is, by resort to chemical reactions that convert the unwanted impurities into readily separable substances.

Suitably prepared, the reactants are reacted with one another; this interaction often includes several steps. Between these steps it may prove necessary again to utilize the mechanisms of heat and mass transfer and some other physical processes. For example, the manufacture of sulphuric acid involves the partial oxidation of sulphur dioxide to sulphur trioxide, following which the feed is allowed to cool, the sulphur trioxide is separated from the feed by absorption, and the remainder is again returned to the oxidation step.

A chemical reaction yields a mixture of the end product(s), by-products, and unreacted reagents. Quite logically, the final step (or steps) has as its objective to separate the mixture, again using heat and mass transfer, and fluid-dynamic phenomena, such as filtration, centrifugation, distillation, absorption, extraction, and so on. The products are sent to storage or for further processing; the unreacted materials are re-used as recycle. The final steps may also include the recovery of waste heat and the treatment of process wastes (both liquid and gaseous) for removal of

whatever values they may carry and as a way of averting any likely damage to the surroundings.

Thus, on the whole a chemical process is a *multifaceted system* consisting of interrelated elements and interacting with the environments.

The elements of this chemical engineering system are the heat and mass transfer, fluid-dynamic, chemical and other mechanisms listed above. They constitute what are known as the *unit operations of chemical engineering*.

An important subsystem of a complex chemical process is the reaction process sometimes classed as a *unit process* or *chemical conversion*. It is one or several chemical operations accompanied by heat, mass and momentum transfer.

Analysis of unit operations and of their interrelations enable the chemical engineer to define the necessary process variables.

The process variables are a set of quantities that define the operating conditions of a reactor or a system of reactors.

The optimal process variables refer to a set of basic quantities (such as temperature, pressure, feed composition, catalyst, etc.) that result in a maximum yield of the end product at the highest rate and at the lowest cost.

Unit operations may take place in various pieces of process plant, such as chemical reactors, absorption and rectification columns or towers, heat exchangers, etc. The interconnection of the various pieces of process plant is known as the *plant layout* and is shown on a suitable *flow diagram*. The development of a rational plant layout and flow diagram is a vital task of chemical engineering.

1.1 Classification of Chemical Reactions Lying at the Basis of Industrial Chemical Processes

Chemistry today knows a great number of chemical reactions widely differing in nature. Many of them are carried out in industrial reactors and as such they become a subject of study by chemical engineering.

In order to facilitate the study of phenomena close in nature, it is customary in science to classify them by some general attributes. These attributes are many and diverse, and so are the classifications of chemical reactions. Some classifications are mainly used in chemistry (inorganic, organic, etc.), others in chemical engineering, still others are common to both.

Let us name some classifications that are used in chemical engineering.

When designing a reactor or choosing forms of control for a given process, an important factor is the *phase composition of the feed*. Accordingly, there may be *homogeneous* and *heterogeneous chemical reactions*.

In homogeneous reactions, the reactants and the products are in the same phase (liquid or gaseous). For example, the oxidation of nitrogen oxide by atmospheric oxygen in the manufacture of nitric acid is a gas-phase reaction, while esterification (the formation of esters from organic acids and alcohols) is a liquid-phase reaction.

In a heterogeneous reaction, at least one of the reactants or products is in a phase different from that of the remaining reactants or products. There are two-phase (or binary) systems, such as 'gas-liquid', 'gas-solid', 'liquid-solid', 'liquid-liquid' (involving two immiscible liquids), 'solid-solid', and various combinations of three-phase (or ternary) systems.

Another form of classification is by the mechanism involved in a reaction. There are *simple* (single-step) and *complex* (or multi-step) reactions, notably concurrent (or parallel), consecutive (or series), and concurrent-consecutive (or mixed).

A simple reaction is that which can be carried to completion by overcoming only one energy barrier (a single-step reaction).

A complex reaction includes several concurrent (parallel) or consecutive (series) steps or both.

Single-step reactions are an extremely rare occurrence in practice. However, some complex reactions proceed via a chain of intermediate steps which can conveniently be treated as *formally simple reactions*. This approach is legitimate when no intermediate reaction products or, simply, *intermediates* can be discerned under a given set of conditions.

A further form of classification is according to the number of molecules that take part in reaction. This is known as the *molecularity* of a reaction, and there may be mono-, bi-, and tri-molecular reactions.

Still another form of classification is according to the *overall reaction order* which is the sum of the powers to which all the reactant concentrations appearing in the rate equation (or expression) are raised. Accordingly, we have first-order, second-order, third-order, and fractional-order reactions.

The rate of a reaction may or may not be changed deliberately by adding suitable substances, called *catalysts*. Accordingly, there are *catalytic* (or *catalyzed*) and *noncatalytic* (or *uncatalyzed*) reactions and, by the same token, catalytic or noncatalytic chemical engineering processes. Most chemical reactions serving as the basis of industrial chemical technology are catalytic reactions.

Finally, reactions may be classed according to their *thermal effect*, that is, according as they give off or absorb heat to or from the surroundings. The former are called *exothermic reactions*, and the latter are called *endothermic reactions*. During an exothermic reaction ($Q > 0$), the enthalpy of the reacting system decreases ($\Delta H < 0$). During an endothermic reaction ($Q < 0$), the enthalpy of the reacting system increases ($\Delta H > 0$).

1.2 Efficiency Criteria of a Chemical Process

An idea about the efficiency of any industrial activity can above all be formed from its economics — first cost, overheads, other expenses, etc.

Naturally, the final judgement as to the efficiency of a chemical process is passed on the basis of the above criteria. However, they characterize the process as an economic entity or, rather, its final result without going into a detailed consideration of the process as such.

If we wish to assess the efficiency of the various steps or stages of a chemical engineering process, we need, in addition to the general economic criteria, to have those which reflect the chemical and physico-chemical aspects of what happens in the various pieces of the process plant used.

These criteria are, above all, *fractional conversion*, *product yield*, and *selectivity*. They describe, each from a particular angle, how completely the potentialities of a given chemical reaction have been utilized.

✓ **Fractional conversion.** It shows how fully a given chemical engineering process utilizes the starting material(s).

More precisely, **fractional conversion is the fraction of a reactant that has undergone chemical change at a particular stage of the reaction process.** //

The fractional conversion of reactant J is

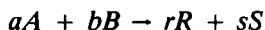
$$x_J = (n_{J,0} - n_J)/n_{J,0} \quad (1.1)$$

where:

$$\begin{aligned} x_J &= \text{fractional conversion of reactant } J \\ n_{J,0} &= \text{quantity of reactant } J \text{ in the feed} \\ n_J &= \text{quantity of reactant } J \text{ in the exit stream or in the reactor} \end{aligned}$$

Most often, a chemical reaction involves not one but two (or even more) reactants. The fractional conversion may be calculated for the first, second, or third reactant*

If the reaction in question is



then

$$\left. \begin{aligned} x_A &= (n_{A,0} - n_A)/n_{A,0} \\ x_B &= (n_{B,0} - n_B)/n_{B,0} \end{aligned} \right\} \quad (1.2)$$

Using the fractional conversion, we may readily find the quantity of products R and S formed as a result of the reaction not complicated by any side reactions. The quantities of products, n_R and n_S , are connected to the

* It is usually of practical importance to consider the fractional conversion of the *limiting reactant*. — *Translator's note.*

quantities of reactants by the following relations:

$$n_R = (n_{A,0} - n_A)(r/a) = (n_{A,0} - n_A)\psi_{AR} \quad (1.3)$$

$$n_S = (n_{A,0} - n_A)(s/a) = (n_{A,0} - n_A)\psi_{AS} \quad (1.4)$$

or

$$n_R = (n_{B,0} - n_B)(r/b) = (n_{B,0} - n_B)\psi_{BR} \quad (1.5)$$

$$n_S = (n_{B,0} - n_B)(s/b) = (n_{B,0} - n_B)\psi_{BS} \quad (1.6)$$

where ψ_{AR} , ψ_{BR} , ψ_{AS} , and ψ_{BS} are the normalizing coefficients that take care of the stoichiometry of the reaction and are equal to the ratio between the stoichiometric coefficient of the product in the equation of the reaction to the stoichiometric coefficient of the reactant.

Since, in view of Eqs. (1.2),

$$n_{A,0} - n_A = n_{A,0}x_A$$

and

$$n_{B,0} - n_B = n_{B,0}x_B$$

it follows that

$$n_R = n_{A,0}x_A\psi_{AR} = n_{A,0}x_A(r/a) \quad (1.7)$$

or

$$n_R = n_{B,0}x_B\psi_{BR} = n_{B,0}x_B(r/b) \quad (1.8)$$

Proceeding in a similar way, we may present the quantity of reactant S as a function of the fractional conversion of one of the reactants.

It follows from Eqs. (1.7) and (1.8) that

$$n_{A,0}x_A\psi_{AR} = n_{B,0}x_B\psi_{BR} \quad (1.9)$$

Hence,

$$x_B = \frac{n_{A,0}\psi_{AR}}{n_{B,0}\psi_{BR}} x_A = \frac{n_{A,0}/n_{B,0}}{a/b} x_A \quad (1.10)$$

Equation (1.10) connects the fractional conversions of reactants A and B and enables one to calculate the unknown conversion of one of the reactants when that of the other is known. If

$$n_{A,0}/n_{B,0} = a/b \quad (1.11)$$

which states that reactants A and B are taken for a reaction in a stoichiometric ratio (the ratio between the quantities of reactants A and B is the same as that between their stoichiometric coefficients in the equation of the reaction), it follows that the fractional conversions x_A and x_B are equal, that is, $x_A = x_B$. If

$$(n_{A,0}/n_{B,0}) > (a/b) \quad (1.12)$$

which states that reactant A is taken in excess, then, as follows from Eq. (1.10), $x_A < x_B$. Finally, if

$$(n_{A,0}/n_{B,0}) < (a/b) \quad (1.13)$$

which states that reactant B is taken in excess, then $x_A > x_B$.

It is important to remember that the fractional conversion is the fraction of the original quantity of a reactant that has been converted to a reaction product. Therefore, the range of x is defined as

$$0 \leq x \leq 1 \quad (1.14)$$

and, if one of the reactants (say, reactant B) is taken in excess, then, subject to Eqs. (1.10) and (1.13), it will always be that $x_B < 1$, even though $x_A = 1$.

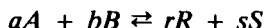
As a rule, the least expensive reactant is taken in excess when the composition of the feed is chosen, so that the more expensive reactant could be better utilized. The less expensive reactant may be water, air, etc.

It is not always possible to utilize a reactant completely (that is, to achieve a condition in which $x = 1$). Most chemical reactions are reversible. For reversible reactions proceeding under a given set of conditions, the limiting state is a state of chemical equilibrium. This state corresponds to the maximum fractional conversion attainable under these conditions

$$x_{A,e} = (n_{A,0} - n_{A,e})/n_{A,0} \quad (1.15)$$

where $n_{A,e}$ is the quantity of reactant A at equilibrium *.

Accordingly, for the reversible reaction



the maximum obtainable quantity of product R is

$$n_{R,e} = n_{A,0} x_{A,e} \psi_{AR} \quad (1.16)$$

where $n_{R,e}$ is the equilibrium quantity of product R .

If the reaction volume V is a constant quantity, the amounts of all reactants and products in the above relations may be replaced with the respective molar concentrations. For example,

$$x_A = \frac{n_{A,0} - n_A}{n_{A,0}} = \frac{n_{A,0}/V - n_A/V}{n_{A,0}/V} = \frac{C_{A,0} - C_A}{C_{A,0}} \quad (1.17)$$

and

$$C_R = n_R/V = C_{A,0} x_A \psi_{AR} \quad (1.18)$$

Yield. The fractional conversion of a reactant tells us how efficiently a process is conducted from the view-point of the utilization of the starting material. However, it does not tell us how efficient it is in terms of the reaction product. To fill this need, one more efficiency criterion is used, called *yield*.

* Here and elsewhere the subscript 'e' stands for 'equilibrium' and is assigned to the quantities existing at equilibrium.

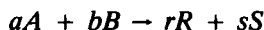
The yield of a product is the ratio of the quantity of product actually obtained to its maximally obtainable quantity.

Symbolically, the yield is

$$\Phi_R = n_R / n_{R,\max} \quad (1.19)$$

The value of $n_{R,\max}$ depends on the type of reaction involved. Let us take a closer look at some of them.

a. The nonreversible chemical reaction



Let us assume that reactant A is taken in an amount corresponding to the stoichiometric ratio between reactants A and B or in less than its stoichiometric amount such that

$$n_{A,0} / n_{B,0} \leq a / b$$

Then the maximally obtainable amount of product R will result if all of reactant A ($n_{A,0}$) reacts with reactant B , that is,

$$n_{R,\max} = n_{A,0} \psi_{AR} = n_{A,0} (r/a) \quad (1.20)$$

Then,

$$\Phi_R = n_R / n_{A,0} \psi_{AR} \quad (1.21)$$

Since, in accord with Eq. (1.7),

$$n_R = n_{A,0} x_A \psi_{AR}$$

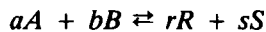
it follows that

$$\Phi_R = n_{A,0} x_A \psi_{AR} / n_{A,0} \psi_{AR} = x_A \quad (1.22)$$

Or, in words, for simple reactions the yield of the product is equal to the fractional conversion of the reactant.

For other reactions, however, the yield of a product is not equal to the fractional conversion of a reactant.

b. The reversible chemical reaction



The maximally obtainable quantity of product R is that which can theoretically be produced at equilibrium, that is,

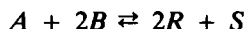
$$n_{R,\max} = n_{R,e}$$

Subject to Eqs. (1.7) and (1.16), we get

$$\Phi_R = \frac{n_R}{n_{R,e}} = \frac{n_{A,0} x_A \psi_{AR}}{n_{A,0} x_{A,e} \psi_{AR}} = x_A / x_{A,e} \quad (1.23)$$

Thus, for reversible reactions the yield of a product is equal to the ratio of the actual conversion to the equilibrium conversion under a given set of conditions.

Example 1.1 Let the reaction be



The starting quantities of reactants are $n_{A,0} = 10$ kmol and $n_{B,0} = 25$ kmol. The stream leaving the reactor contains 12 kmol of product R . It is known that under the existing set of conditions the equilibrium feed contains 2.5 kmol of reactant A . Determine the yield of product R , that is Φ_R .

In accord with Eq. (1.23),

$$\Phi_R = x_A / x_{A,e}$$

$$\text{Yield} = \frac{12}{(10 - 2.5) \times 2} = 0.8$$

In accord with Eq. (1.1) and subject to Eq. (1.3), we have

$$x_A = \frac{n_R / \psi_{AR}}{n_{A,0}} = \frac{12/2}{10} = 0.6$$

For this reaction,

$$\psi_{AR} = r/a = 2/1 = 2$$

The conversion at equilibrium is

$$x_{A,e} = \frac{n_{A,0} - n_{A,e}}{n_{A,0}} = \frac{10 - 2.5}{10} = 0.75$$

Hence,

$$\Phi_R = x_A / x_{A,e} = 0.6/0.75 = 0.8$$

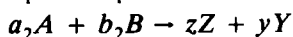
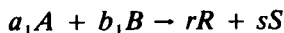
As an alternative, the yield of product R in the above example can be found by finding

$$n_{R,e} = (n_{A,0} - n_{A,e})\psi_{AR} = 15 \text{ kmol}$$

and then using Eq. (1.19):

$$\Phi_R = n_R / n_{R,e} = 12/15 = 0.8$$

c. Concurrent (parallel) and consecutive (series) reactions. Suppose that two reactions are going on concurrently to yield product R and by-products, that is, the products of a side reaction:



The maximum amount of product R can be obtained if reactant A taken in the proportion $n_{A,0}/n_{B,0} \leq a_1/b_1$ will solely follow the route that yields the desired product. Then

$$\Phi_R = n_R/n_{A,0}\psi_{AR} \quad (1.24)$$

It is important to remember that n_R cannot be expressed in terms of the fractional conversion and the starting amount of reactant A in the case of a complex reaction because reactant A will then be used up in two reactions, one yielding the desired product and the other, a by-product.

A similar form will be taken by the expression for the yield of the desired product R in the case of consecutive (series) reactions, such as



In the case of reversible concurrent and consecutive reactions, the maximum obtainable amount of desired product R will be that which would be obtained if reactant A were used up solely in the desired reaction and if there were no side reactions at equilibrium.

Thus, for reversible complex reactions

$$\Phi_R = \frac{n_R}{(n_{A,0} - n_{A,e})\psi_{AR}} = \frac{n_R}{n_{A,0}x_{A,e}\psi_{AR}} \quad (1.25)$$

Similarly to the fractional conversion of a reactant, the yield of a product for constant-volume reaction systems may be defined as the ratio of concentrations. It should likewise be remembered that yield, expressed as a fraction of some limiting value, can range from 0 to 1.

Selectivity. The yield of a product characterizes the result as a fraction of some limit. It is no less important to evaluate the actual situation, that is, to form a quantitative estimate of how effective the desired reaction is in comparison with the likely side reactions.

The relevant criterion is *selectivity*. Similarly to the two previous criteria, selectivity is expressed as a fraction of unity.

Total or integral selectivity, φ , is the ratio between the amount of reactant used up in a desired reaction, and the total amount of the same reactant used up during the overall reaction.

Point or differential selectivity, φ' , is the ratio between the rate at which the reactants are converted to the desired product, and the overall rate of consumption of the reactants

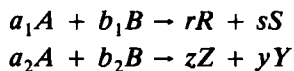
$$\varphi' = w_{r(A \rightarrow R)} / w_{rA} \quad (1.26)$$

where $w_{r(A \rightarrow R)}$ = rate of consumption of reactant A in the reaction which yields the desired product

w_{rA} = overall rate of consumption of reactant A

The use of differential selectivity in the analysis of chemical engineering processes will be taken up in more detail in Chap. 3. Here we will consider only total selectivity.

For the reactions



the total selectivity with respect to product R may be expressed in terms of the quantity of product R obtained and the total quantity of reactant A used up in the reaction.

The stoichiometric quantity of reactant A that will yield a given quantity of product R is

$$n_R/(r/a) = r_R/\psi_{AR}$$

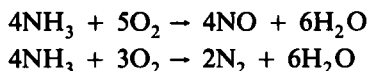
Then the total selectivity φ will be

$$\varphi = \frac{n_R/\psi_{AR}}{n_{A,0} - n_A} \quad (1.27)$$

The denominator in Eq. (1.27) may be replaced with the quantities of products produced by the desired and side reactions, subject to the normalizing stoichiometric factors ψ :

$$\begin{aligned}n_{A,0} - n_A &= n_R/\psi_{AR} + n_Z/\psi_{AZ} \\ &= n_S/\psi_{AS} + n_Y/\psi_{AY} \\ &= n_R/\psi_{AR} + n_Y/\psi_{AY} = \dots\end{aligned} \quad (1.28)$$

Example 1.2 As an example, let us consider the concurrent (or parallel) reactions



The reaction that yields the desired product is that which produces nitrogen oxide, NO.

The selectivity can be found from the quantities of desired product (nitrogen oxide) and of by-product (nitrogen) in the exit stream from the reactor:

$$\varphi = \frac{n_{\text{NO}}/1}{n_{\text{NO}}/1 + n_{\text{N}_2}/0.5} = \frac{n_{\text{NO}}}{n_{\text{NO}} + 2n_{\text{N}_2}}$$

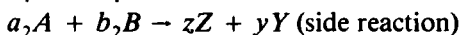
where

$$\psi_{\text{NH}_3-\text{NO}} = 4/4 = 1$$

and

$$\psi_{\text{NH}_3-\text{N}_2} = 2/4 = 0.5$$

The yield of the desired product, the fractional conversion of the reactant, and the selectivity are connected by a simple relation. To begin with, let us take as an example two nonreversible concurrent reactions such as



In accord with Eq. (1.24), the yield of product R is

$$\Phi_R = n_R/n_{R,\max} = n_R/n_{A,0}\psi_{AR} \quad (1.29)$$

The quantity of product R actually obtained from the reaction can be expressed in terms of selectivity by using Eq. (1.27)

$$n_R = \varphi(n_{A,0} - n_A)\psi_{AR} = \varphi n_{A,0}x_A\psi_{AR} \quad (1.30)$$

On substituting Eq. (1.30) into Eq. (1.29), we obtain

$$\Phi_R = \frac{\varphi n_{A,0}x_A\psi_{AR}}{n_{A,0}\psi_{AR}} = \varphi x_A \quad (1.31)$$

When concurrent reactions are reversible, the maximum quantity of product R that could be obtained if there were no side reaction depends on the conditions of equilibrium. Then the yield of the product should be found by using Eq. (1.25). On substituting the actual quantity of product R , as expressed with the aid of Eq. (1.30), in Eq. (1.25), we will have a more general equation relating the yield, selectivity and fractional conversion

$$\left. \begin{aligned} \Phi_R &= \varphi n_{A,0}x_A\psi_{AR}/n_{A,0}x_{A,e}\psi_{AR} \\ \text{or} \quad \Phi_R &= \varphi x_A/x_{A,e} \end{aligned} \right\} \quad (1.32)$$

It follows from Eqs. (1.31) and (1.32) that when choosing the operating conditions for complex chemical reactions, it is not enough to assure only a high conversion or only a high selectivity — the high yield of the reaction product is a function of both.

The optimal values of yield, selectivity and conversion are as a rule those which assure a maximum economical efficiency of the process.

Throughput and production rate. *Throughput* is a very important efficiency criterion of individual items of equipment, installations, or complete plants.

Throughput is the quantity of product obtained per unit time

$$T = n_R/\tau \quad (1.33)$$

where T = throughput

n_R = quantity of product

τ = time

Throughput may be expressed in kilograms per hour, tonnes per day, tonnes per year, etc. For example, the throughput of a state-of-the-art ammonia synthesis unit is 1360 tonnes/day of ammonia, and that of a sulphuric-acid unit, 500,000 tonnes/yr. Sometimes, throughput is stated in terms of the quantity of raw materials processed per unit time. For example, the throughput of a typical pyrite roaster is 450 tonnes/day.

If we know the concentration of the product in the stream leaving a reactor and the volumetric flow rate of the feed, the throughput can conveniently be found by the equation

$$T = C_R v$$

where C_R = concentration of the product

v = volumetric flow rate of the feed

The maximum throughput that can be shown by a given item of plant is usually referred to as its *capacity*, or *design capacity*. In Soviet practice, major emphasis is placed on the use of large-capacity units as this leads to reduced capital costs and increased productivity.

Production rate (sometimes called *intensity*) comes in where it is desired to compare units of plant in which the same chemical reactions or processes are carried out.

Production rate is defined as the throughput per unit of some quantity characterizing the geometry of the equipment, such as its volume, cross-sectional area, etc.

For example,

$$I = T/V = n_R/V\tau \quad (1.35)$$

where V is the volume of the item of equipment involved. Production rate is expressed in kilograms per hour per cubic metre ($\text{kg hr}^{-1} \text{m}^{-3}$), tonnes per day per square metre ($\text{t day}^{-1} \text{m}^{-2}$), etc.

When new chemical manufacturing processes are being developed or existing ones are being revamped, it is always sought to achieve the highest possible production rate. The production rate of an item of plant can often be enhanced by effecting the associated process under conditions that assure a high rate.

When analysing the performance of a catalytic reactor, it is customary to refer its throughput to the unit of volume or mass of the catalyst used in the reactor. This quantity numerically equal to the quantity of product obtained per unit volume or mass of catalyst is referred to as the capacity of the catalyst.

Chapter Two

THERMODYNAMIC ANALYSIS OF CHEMICAL PROCESSES

Thermodynamic analysis is an important aspect in the design of chemical processes. Above all, it tells the designer whether the contemplated process is feasible. It enables him to make a preliminary choice of the process variables, to determine the equilibrium composition of the feed, and to calculate the theoretically achievable reactant conversions and product yields. Also, it shows what thermal effects he may or should expect (among them the heat of the reaction, the heat of physical changes, etc.), which is essential in setting up the energy and material balances involved.

In its widest sense, thermodynamics is a science which deals with various forms of energy conversion. Energy is inseparable from the motion of matter. Motion is associated with matter as a form of its existence, while energy is a measure of the motion of matter. The fact that any interconversion of the various forms of the motion of matter leaves the associated momentum unaffected is the essence of the laws of conservation and conversion of energy.

The key concepts of thermodynamics are the heat of a process and work, both of which are the forms of energy transfer. The conversion of heat into work or the other way around is usually carried out in a thermodynamic system by agency of what is known as the *working fluid*. A thermodynamic system is called *homogeneous* if its properties are the same throughout the system. The set of physical properties characterizing the working fluid (or a thermodynamic system) under given conditions is called the *state of the fluid* (or *of the system*). The quantities determining the state of a thermodynamic system are referred to as *thermodynamic variables* or *properties*. They are temperature, pressure, specific volume, density, molar volume, specific internal energy, and some others.

The variables (and also the properties) of a thermodynamic system may be divided into two general classifications. Those directly dependent on the mass (or the quantity of material) in the system or the working fluid in question are called *extensive properties*. These are volume, internal energy, enthalpy, entropy, and some others. The extensive properties are additive. The properties which are independent of the mass of a thermodynamic system are called *intensive properties*; only the intensive properties are the thermodynamic variables of state or, simply, the *state variables of a thermodynamic system*. In this classification are found temperature, pressure, and also the extensive properties referred to unit of mass, volume or quantity of material. A change in the intensive properties for the purpose of speeding up chemical processes is called intensification.

2.1 Equilibrium of Chemical Reactions

When an amount of energy is put into or withdrawn from a thermodynamic system in the form of heat or work, this brings about a change in the state of the system (in the values of its variables). This change is called a *thermodynamic process*. A change during which the system passes from an initial to a final state involves a sequence of states which is called the *thermodynamic path* of the system for that change. If this sequence is a continuous chain of equilibrium states, the change, or process, is called an equilibrium one. An *equilibrium state* is that which is attained by a system under constant external conditions which implies the time invariance of the thermodynamic variables and the non-existence of flows of matter and heat in the system.

A state of steady equilibrium is that which is described by the following general conditions:

(1) The equilibrium state of the system remains unchanged with time under constant external conditions.

(2) The equilibrium has the property of mobility (which means that the state of equilibrium will spontaneously restore itself after removal of the external influence that caused the departure of the system from a state of equilibrium).

(3) The equilibrium has a dynamic property (which means that a state of equilibrium is attained and maintained owing to the fact that the forward and reverse processes proceed at the same rate).

(4) The state of equilibrium can be approached from either side.

(5) The Gibbs free energy, G , has a minimal value in constant-pressure/constant-temperature processes and the Helmholtz free energy, F , has a minimal value in isochoric/isothermal processes ($dG = 0$, $d^2G > 0$; $dF = 0$, $d^2F > 0$).

Using the above general conditions, we can readily deduce specific conditions for a state of chemical equilibrium.

As a rule, chemical reactions are reversible: a *forward reaction* (that is, one between the original reactants) is accompanied by a *reverse* (or *backward*) reaction (that is, one between the reaction products). As the process goes on, the rate of the forward reaction decreases while that of the reverse reaction increases. At some instant, the rates of the two reactions become the same, and a state of chemical equilibrium is established. Chemical equilibrium is characterized by the fact that, given constant external conditions, the number of molecules in the substances that make up the system remains unchanged. Since one of the conditions for a state of equilibrium to exist at constant temperature, T , and pressure, p , is a minimal value of the Gibbs free energy (or a zero free energy change, $dG = 0$), it means that the following equality must be likewise satisfied at chemical equilibrium:

$$\sum \mu_j dn_j = 0 \quad (2.1)$$

where μ_j = chemical potential of component J
 n_j = number of moles of component J

As will be recalled, the chemical potential is defined as

$$\mu_j = (\partial G / \partial n_j)_{T,p,n_j} = \bar{G}_j \quad (2.2)$$

When μ_j has a high positive value, this is an indication that the species involved are highly reactive.

Mass action law *. For the first time the fact that the direction of a chemical process depends on the concentrations of the participating reactants was established by N.N. Beketov of Russia in 1865 on the basis of conclusive experiments. In mathematical form, this law was stated by C. Guldberg and P. Waage in 1867.

Let us derive this law (alternatively called the *law of mass action*) from kinetic considerations, taking as an example the following homogeneous reaction



As the reader surely knows from a course in general chemistry, the rate of the forward reaction is proportional to the product of the concentrations of reactants A and B :

$$\bar{w} = k_1 C_A^a C_B^b$$

while the rate of the reverse reaction is proportional to the product of the concentrations of reaction products R and S :

$$\bar{w} = k_2 C_R^r C_S^s$$

Each concentration is raised to a power equal to the stoichiometric coefficient (the number of molecules) of the respective component taking part in the reaction. Since the rates of the forward and reverse reactions at chemical equilibrium are the same

$$k_1 C_{A,e}^a C_{B,e}^b = k_2 C_{R,e}^r C_{S,e}^s \quad (2.3)$$

it follows that

$$k_1/k_2 = C_{R,e}^r C_{S,e}^s / C_{A,e}^a C_{B,e}^b \quad (2.4)$$

where $C_{A,e}$, $C_{B,e}$, $C_{R,e}$, and $C_{S,e}$ are the respective equilibrium concentrations.

The ratio of the rate constants, k_1/k_2 , is called the *equilibrium constant* and is given the symbol K_C . Hence, we get the following expression for the law of mass action:

$$K_C = k_1/k_2 = C_{R,e}^r C_{S,e}^s / C_{A,e}^a C_{B,e}^b \quad (2.5)$$

As follows from Eq. (2.5), the equilibrium constant is independent of concentration because a change in the concentration of one participant in

* Originally, the term 'active masses' was used instead of concentrations, so the law should have been called 'the law of equilibrium concentrations'.

the reaction brings about changes in the concentrations of all the other reactants and products so that K_C remains numerically unchanged. Thus, the primary objective of the mass action law is to establish the connection between the equilibrium concentrations of all the reactants and products.

In the case of gas-phase reactions, the equilibrium constant is expressed in terms of partial pressures:

$$K_p = p_{R,e}^r p_{S,e}^s / p_{A,e}^a p_{B,e}^b \quad (2.6)$$

Since, in accord with the Clapeyron equation,

$$p_j = C_j RT$$

it follows that

$$K_C = K_p (RT)^{-\Delta n} \quad (2.7)$$

where

$$\Delta n = (r + s - a - b)$$

is the change in the number of moles of the gaseous reactants and products on reaction.

Alternatively, the equilibrium constant may be expressed in terms of the ratio of mole fractions, N_j , of the participants in the reaction:

$$K_N = N_{R,e}^r N_{S,e}^s / N_{A,e}^a N_{B,e}^b \quad (2.8)$$

or in terms of the number of moles of the components, n_j :

$$K_n = n_{R,e}^r n_{S,e}^s / n_{A,e}^a n_{B,e}^b \quad (2.9)$$

For real systems, the equilibrium constant is expressed in terms of either *fugacity* f or *activity* a . Thus, for reaction (1) that we have chosen as an example,

$$K_f = f_{R,e}^r f_{S,e}^s / f_{A,e}^a f_{B,e}^b \quad (2.10)$$

or

$$K_a = a_{R,e}^r a_{S,e}^s / a_{A,e}^a a_{B,e}^b \quad (2.11)$$

At low pressures and at practically any temperature,

$$K_a = K_f = K_p = K_N p^{\Delta n} = K_n \left(\frac{p}{n_R + n_S + n_A + n_B} \right)^{\Delta n} \quad (2.12)$$

The equilibrium constant and the Gibbs free energy. The van't Hoff isotherm. In the case of reaction (1), the free energy change is given by

$$\Delta G = r\mu_R + s\mu_S - a\mu_A - b\mu_B \quad (2.13)$$

Because it has been assumed that all the participants in the reaction are ideal (or perfect) gases, then at constant temperature

$$\mu_j = \mu_j^o + RT \ln p_j \quad (2.14)$$

where μ_j^o is the standard chemical potential of material J (the "o" sign indicates that a standard state is meant).

On substituting the chemical potentials expressed in accord with Eq. (2.14) into Eq. (2.13) and collecting the terms, we get

$$\Delta G = (r\mu_R^\circ + s\mu_S^\circ - a\mu_A^\circ - b\mu_B^\circ) + RT(r \ln p_R + s \ln p_S - a \ln p_A - b \ln p_B) \quad (2.15)$$

Because the first expression in parentheses is ΔG° , or the standard free energy change, it follows that

$$\Delta G = \Delta G^\circ + RT \ln (p_R^r p_S^s / p_A^a p_B^b) \quad (2.16)$$

At chemical equilibrium, $\Delta G = 0$, and so

$$\Delta G^\circ = -RT \ln (p_{R,e}^r p_{S,e}^s / p_{A,e}^a p_{B,e}^b) \quad (2.17)$$

The standard Gibbs free energy at a given temperature is a constant which is typical of a given reaction. Therefore the expression under the logarithm sign must likewise be a constant. On giving it the symbol K_p , we obtain

$$\Delta G^\circ = -RT \ln K_p \quad (2.18)$$

It is to be remembered that the expressions for the equilibrium constant (K_p , K_C) include relative dimensionless quantities (say, pressures per unit standard pressure), rather than the absolute values of equilibrium pressures or concentrations of the reactants and products.

Equation (2.18) is known as the *van't Hoff isotherm*. It relates in general form the Gibbs free energy and the equilibrium constant which can be calculated, if one knows the standard free energy change, ΔG° .

The standard Gibbs free energies of formation for many thousand chemical compounds are summarized in tables of thermodynamic properties and can be found in handbooks and other reference sources. If such tables are not available, ΔG° can be found by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.19)$$

where ΔH° = standard enthalpy change

ΔS° = standard entropy change

The values of the last two thermodynamic properties can likewise be found in tabulated form in reference sources and handbooks.

From the order and sign of ΔG° , one can readily predict the equilibrium position for a reaction. If $\Delta G^\circ \ll 0$, the equilibrium is shifted to the right, the yield of the product is large, and the equilibrium constant is high. On the contrary, if $\Delta G^\circ \gg 0$, the equilibrium is shifted to the left, the yield is small, and $K_p \ll 1$.

A reaction will be favoured to proceed to the right by large negative values of ΔH° (that is, by a substantial thermal effect) and large positive values of ΔS° (that is, by an increase in entropy). The entropy term enters Eq. (2.19) as the product $T\Delta S^\circ$. Therefore, a rise in temperature enhances

the influence of a change in entropy. At equilibrium

$$\Delta H^\circ = T\Delta S^\circ$$

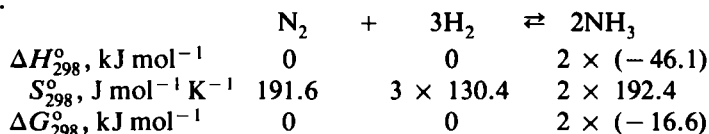
at any temperature, that is, the energy and entropy factors are equal in their effect on the reaction.

On solving Eqs. (2.18) and (2.19) simultaneously for K_p , we get

$$\begin{aligned} K_p &= \exp(-\Delta G^\circ/RT) \\ &= \exp(-\Delta H^\circ/RT) \exp(\Delta S^\circ/R) \end{aligned} \quad (2.20)$$

From analysis of Eq. (2.20) it is seen that for exothermic reactions ($\Delta H < 0$) which proceed with an increase in entropy, $K_p > 1$ and $\Delta G^\circ < 0$. Endothermic reactions ($\Delta H > 0$), which proceed with a decrease in entropy ($\Delta S^\circ < 0$), cannot go on spontaneously. If ΔH° and ΔS° have the same sign, the thermodynamic feasibility of the reaction will be determined by the specific values of ΔH° , ΔS° , and T .

Taking ammonia synthesis as an example, let us see how ΔH° and ΔS° can affect the course of the process (the values of the thermodynamic functions for the participants of the process are given below the equation of the reaction):



Thus, for the reaction in question,

$$\begin{aligned} \Delta H_{298}^\circ &= -92.2 \text{ kJ mol}^{-1} \\ \Delta S_{298}^\circ &= -198.0 \text{ J mol}^{-1} \text{ K}^{-1} \\ T\Delta S_{298}^\circ &= -59 \text{ kJ mol}^{-1} \\ \Delta G_{298}^\circ &= -33.2 \text{ kJ mol}^{-1} \end{aligned}$$

It is seen from the above data that the change in entropy is negative and does not favour the reaction. At the same time, however, there is a substantial negative change in enthalpy, ΔH° , so the reaction is feasible after all. As calorimetric data show, an increase in temperature renders the reaction still more exothermic (at 725K, $\Delta H = -113 \text{ kJ mol}^{-1}$). When ΔS° is negative, however, a rise in temperature substantially reduces the thermodynamic feasibility of the reaction.

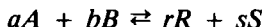
2.2 Le Chatelier's Principle

The position of equilibrium is always dependent on external conditions. Since, however, the latter cannot remain unchanged, the equilibrium is shifted, or upset, in the long run. The effect of changes in the external

conditions on the position of equilibrium, known as *Le Chatelier's principle*, may be formulated as follows.

If a change occurs in one of the conditions of a system in equilibrium, the system will adjust itself so as to annul, as far as possible, the effect of that change*.

Let us consider the reaction



where reactants A and B , and products R and S are ideal gases. At equilibrium, the following equality holds:

$$\ln \frac{p'_{R,e} p'^s_{S,e}}{p^a_{A,e} p^b_{B,e}} = -\Delta G^\circ / RT = \ln K_p \quad (2.21)$$

If the constraint applied is such that the value of one of the terms in the equality, say, $\Delta G^\circ / RT$ or $p'_{R,e} p'^s_{S,e} / p^a_{A,e} p^b_{B,e}$, changes, the equilibrium is modified so that the system is no longer in a state of equilibrium. As a result, the system will tend towards a new state of equilibrium characterized by other values of the equilibrium partial pressures of the reactants and products.

Since at equilibrium the rates of the forward and reverse reactions are equal, it may be said that the equilibrium is modified when the applied constraint affects the rates of the forward and reverse reactions differently. This departure from equality between the reaction rates causes the system to move to a new state of equilibrium where the rates of the forward and reverse reactions become equal again, but they will be different from the original values.

The effect of pressure. The manner in which pressure affects the equilibrium of chemical reactions depends on the sign taken by the difference in the number of moles of the gaseous reactants, Δn , or by the change in volume, ΔV .

In gas-phase reactions where the number of moles of the products exceeds that of the reactants, that is, $\Delta n > 0$, a rise in pressure will have an unfavourable effect. The equilibrium of the reaction will be shifted to the right by a decrease in pressure. On the contrary, if a reaction proceeds with a decrease in the number of moles of the reactants ($\Delta n < 0$), it will be advantageous to raise the pressure — it will shift the equilibrium of the reaction towards the formation of products.

The position of equilibrium is increasingly more sensitive towards changes in pressure when a reaction (a process) is accompanied by a

* Sometimes, *Le Chatelier's principle* is stated in a somewhat different form:

If a system is subjected to a constraint whereby the equilibrium is modified, a change takes place, if possible, which partially annuls the constraint. — *Translator's note.*

sizeable change in volume (the number of moles). The volume of the reaction mixture can change appreciably only in reactions involving gases or when at least one of the participants is in the gas (or vapour) phase. Quantitatively, the effect of pressure on equilibrium is evaluated by Eq. (2.12).

The effect of inert gases. The addition of an inert gas to a system at constant pressure is equivalent to a reduction in the overall pressure. If the reaction goes on with a decrease in the number of moles ($\Delta n < 0$), the dilution with an inert gas shifts the equilibrium of the reaction to the left. On the contrary, an increase in the number of moles ($\Delta n > 0$) shifts the equilibrium to the right. Therefore, in chemical manufacturing processes based on reactions for which $\Delta n < 0$ measures are usually taken to avoid the accumulation of inert gases in the system. For example, if a nitrogen-hydrogen-ammonia mixture taken at $p = 100$ MPa contained 10% of an inert gas, this would be equivalent to a reduction of 25 MPa in pressure. In order to maintain a high ammonia yield, the system is "purged" and fresh amounts of feed are added at regular intervals (see Chap. 14).

What has been said about the effect of an inert gas stems directly from *Dalton's law of partial pressures*, which states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases or, mathematically,

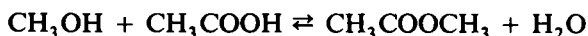
$$p_j = N_j p_{tot} \quad (2.22)$$

As is seen, the effect of dilution (a reduction in N_j) is similar to a reduction in the total pressure, p_{tot} , in the system.

The effect of concentration. In accord with Le Chatelier's principle, when the quantity of some reactant or product in a system is increased, the equilibrium is shifted in a direction so as to reduce the concentration of this reactant or product. Therefore, an excess of the starting materials shifts the equilibrium to the right, and an excess of the products causes the equilibrium to shift to the left. For example, an excess of oxygen increases the equilibrium fractional conversion of SO_2 to SO_3 .

By increasing the concentration of one of the reactants (by maintaining its excess), it is possible to enhance the conversion of the other. This technique is widely used in chemical processing as a way of achieving the complete conversion of an expensive starting material.

In many cases, the equilibrium can be caused to shift to the right by withdrawing the products from the reaction zone, that is, by reducing the concentration of the product. For example, if we add some water-absorbing substances (say, H_2SO_4) to a system effecting the reaction of esterification



we will be able to shift the equilibrium of this reaction to the right.

The effect of temperature. The direction in which the equilibrium can be shifted by a change in temperature depends on the sign of the change. A rise in temperature always favours the accumulation of the substances that are formed by a reaction which requires energy (that is, heat) from the surroundings. In other words, a rise in temperature accentuates the endothermic direction of the process. A fall in temperature exerts an opposite effect, that is, it accentuates the exothermic direction of the reaction.

When the temperature of a process is changed, the equilibrium is shifted in the direction in which the entropy change takes the same sign as the change in temperature. For example, in the ammonia synthesis we considered earlier, $\Delta S < 0$. It therefore follows that a rise in temperature will promote the dissociation of the ammonia while a fall in temperature will promote the synthesis to proceed to the right. The same result is obtained if we consider the sign of the thermal effect that accompanies the reaction ($\Delta H < 0$). A rise in temperature shifts the equilibrium to the left (it accentuates the endothermic direction of the reaction); a fall in temperature acts in the opposite sense.

It is to be noted that the shift in the equilibrium position is increased in proportion to the amount of heat given off or absorbed by the reaction.

To sum up, Le Chatelier's principle enables us to predict the direction of a reaction, that is, to form a qualitative estimate of its equilibrium, without resort to thermodynamics.

2.3 The Equilibrium Constant as a Function of Temperature

The manner in which the equilibrium constant depends on temperature at constant pressure is described by the *van't Hoff isobar*

$$(d \ln K_p / dT)_p = \Delta H^\circ / RT^2 \quad (2.23)$$

where: K_p = equilibrium constant
 ΔH° = standard enthalpy change

It follows from Eq. (2.23) that when ΔH takes a '+' sign (the reaction is endothermic), $d \ln K_p / dT > 0$, and $K_p(T)$ is an increasing function. On the contrary, when ΔH takes a '-' sign (the reaction is exothermic), $d \ln K_p / dT < 0$, and the equilibrium constant decreases with increasing temperature. In both cases, the equivalent concentrations of the participants in the reaction are changed.

Thus, analysis of the above equation shows that it expresses quantitatively the finding that stems from Le Chatelier's principle: An increase in temperature always shifts the equilibrium in the direction of an endothermic reaction.

For processes taking place at constant volume, the manner in which the equilibrium constant varies with temperature is described by the *van't Hoff isochore*

$$(d \ln K_C / dT)_V = \Delta U / RT^2 \quad (2.24)$$

where ΔU is the change in internal energy at constant volume.

The isobar and isochore of a reaction represent variations in the equilibrium constant with temperature in differential form. In practical computations involving various temperatures, these equations have to be integrated. If ΔH is independent of temperature (which is true within a narrow temperature range), Eq. (2.23) can be re-arranged to give the following expression:

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \int_{T_1}^{T_2} (\Delta H / RT^2) dT = (\Delta H / R)(1/T_1 - 1/T_2) \quad (2.25)$$

which is useful for computations involving narrow temperature ranges. If we know the values of ΔH and K_p at some temperature T_1 , we can readily determine the equivalent constant at any other temperature T_2 .

On integrating Eq. (2.23) subject to the condition that the heat given off or absorbed during the reaction is independent of temperature, we may take ΔH out of the integration sign and write the following equation:

$$\ln K_p = -(\Delta H / RT) + B \quad (2.26)$$

where B is the constant of integration.

As will be recalled, in accord with the van't Hoff isotherm,

$$\ln K_p = -(\Delta H^\circ / RT) + (\Delta S^\circ / R) \quad (2.27)$$

Hence,

$$B = \Delta S^\circ / R$$

on the condition that ΔH° and ΔS° are independent of temperature.

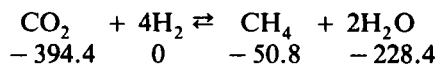
2.4 Estimation of Equilibrium from Thermodynamic Data

Knowledge of the equilibrium constant and of the free energy change is necessary when one is to determine the equilibrium composition of the reaction mixture and the maximum quantity of products that can be obtained.

Finding the equilibrium constants of chemical reactions. The calculation of equilibrium constants for ideal gases from thermodynamic data is based on Eqs. (2.18) and (2.19). These equations relate the equilibrium constant to the free energy change ΔG° which is a function of the standard

enthalpy change, ΔH° , and the standard entropy change, ΔS° . Importantly, we need to know not the absolute values of the thermodynamic functions of the individual participants in a reaction, but their changes. The values of the thermodynamic functions for a large number of simple substances can be found in reference sources. Basing ourselves on reference data, we can calculate the standard free energy change by Hess' law which states that the heat change in a chemical reaction is the same whether the reaction takes place in one or several steps.

Taking as an example the reaction



the values of ΔG_{298}° are known for all the participants in the reaction and written below the equation (in kJ mol^{-1}). Then the ΔG_{298}° for the reaction is

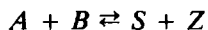
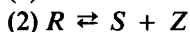
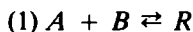
$$\Delta G_{298}^\circ = -50.8 - 2 \times 228.4 + 394.4 = -113.2 \text{ kJ mol}^{-1}$$

Proceeding from the above result, we find the equilibrium constant at 298K

$$\ln K_{p,298} = -\Delta G_{298}^\circ / RT$$

and, in consequence, the equilibrium constant at the temperature of the process.

The equilibrium constants of complex reactions are found by adding together the equilibrium constants of the constituent simple reactions. In this case, it is important to identify and take into account each simple reaction. The individual equilibrium constants must be combined so that, proceeding from the constants known or given in tables, one could express the constants of more complex reactions or deduce the unknown constants from the known ones. Thus, for the consecutive (series) reactions,



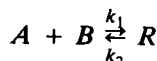
the equilibrium constant of the overall reaction is equal to the product of the equilibrium constants of the constituent simple reactions:

$$\begin{aligned} K_p &= p_{S,e} p_{Z,e} / p_{A,e} p_{B,e} = (p_{S,e} p_{Z,e} / p_{R,e}) (p_{R,e} / p_{A,e} p_{B,e}) \\ &= K_{p_1} K_{p_2} \end{aligned}$$

Accordingly, the total free energy change is equal to the sum of the individual free energy changes:

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_p = -RT \ln (K_{p_1} K_{p_2}) \\ &= \Delta G_1^\circ + \Delta G_2^\circ \end{aligned}$$

Finding the composition of the reaction mixture at chemical equilibrium. To begin with, let us see how the equilibrium constant K_p is related to the equilibrium fractional conversion in the case of the gas-phase reaction



At equilibrium, the reaction mixture will contain $(1 - x_{A,e})$ moles of reactant A , $(1 - x_{A,e})$ moles of reactant B , and $x_{A,e}$ moles of product R per mole of the feed. The total quantity at equilibrium will be

$$1 - x_{A,e} + 1 - x_{A,e} + x_{A,e} = 2 - x_{A,e} \text{ moles}$$

If the total pressure of the system at equilibrium is p , the equilibrium partial pressures will be

$$p_{A,e} = \frac{1 - x_{A,e}}{2 - x_{A,e}} p$$

$$p_{B,e} = \frac{1 - x_{A,e}}{2 - x_{A,e}} p$$

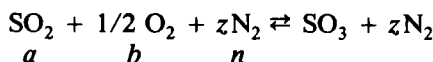
$$p_{R,e} = \frac{x_{A,e}}{2 - x_{A,e}} p$$

Then, the equilibrium constant and the equilibrium conversion will be connected by a relation of the form

$$K_p = \frac{p_{R,e}}{p_{A,e} p_{B,e}} = \frac{x_{A,e} p (2 - x_{A,e})^2}{(2 - x_{A,e})(1 - x_{A,e})^2 p^2} = \frac{x_{A,e} (2 - x_{A,e})}{(1 - x_{A,e})^2 p}$$

Using the above expression, it is an easy matter to determine the equilibrium conversion and, hence, the equilibrium composition of the reaction mixture.

As an example, let us determine the equilibrium constant and the equilibrium conversion from the known values of K_p for the oxidation of sulphur dioxide:



where a , b and n are the numbers of moles of the starting materials, that is, SO_2 , O_2 and N_2 , such that $a + b + n = 1$.

To begin with, we write a material balance around the system at equilibrium:



Number of moles $ax_{A,e} \quad (b - 0.5ax_{A,e}) \quad n \quad (a - ax_{A,e})$

The total number of moles in the mixture at equilibrium is

$$\begin{aligned} \Sigma n_j &= a - ax_{A,e} + b - 0.5ax_{A,e} + n + ax_{A,e} \\ &= 1 - 0.5ax_{A,e} \end{aligned}$$

Now that we know the total number of moles, we may designate the total pressure as p and write the equilibrium pressures of the constituents

$$\begin{aligned} p_{\text{SO}_2,e} &= \frac{a - ax_{A,e}}{1 - 0.5ax_{A,e}} p \\ p_{\text{O}_2,e} &= \frac{b - 0.5ax_{A,e}}{1 - 0.5ax_{A,e}} p \\ p_{\text{SO}_3,e} &= \frac{ax_{A,e}}{1 - 0.5ax_{A,e}} p \end{aligned} \quad (2.28)$$

Then,

$$K_p = p_{\text{SO}_3,e} / p_{\text{SO}_2,e} p_{\text{O}_2,e}^{1/2} = \frac{ax_{A,e}(1 - 0.5ax_{A,e})^{1/2}}{(a - ax_{A,e})(b - 0.5ax_{A,e})^{1/2} p^{1/2}} \quad (2.29)$$

Hence,

$$x_{A,e} = \frac{K_p}{K_p + [(1 - 0.5ax_{A,e})/p(b - 0.5ax_{A,e})]^{1/2}} \quad (2.30)$$

The next step is to determine the composition of the equilibrium mixture on the condition that the feed contained 7% SO_2 , 11% O_2 , and 82% N_2 .

At $T = 650\text{K}$,

$$K_p = 629$$

On substituting the numerical values in Eq. (2.30), we get

$$x_{A,e} = \frac{629}{629 + \left[\frac{1 - 0.5 \times 0.07x_{A,e}}{1(0.11 - 0.5 \times 0.07x_{A,e})} \right]^{1/2}}$$

Hence, using the iteration procedure, we find that $x_{A,e} = 0.994$ and, in consequence, the composition of the equilibrium mixture (in moles) is as follows: SO_3 , 0.069; SO_2 , 0.001; O_2 , 0.041; and N_2 , 0.889.

2.5 Thermodynamic Analysis

The chemical engineer needs to know the laws of thermodynamics not only because he has to carry out thermodynamic analysis so as to be able to predict the likely outcomes of a given chemical transformation, to define the range of pressure and temperature within which the process involved can be run to advantage and to calculate the equilibrium composition of the products, but also because he must be able to evaluate the energetic efficiency of the process he is contemplating or is busy with. This is where thermodynamic analysis comes into the picture. Thermodynamic analysis is based on a relatively limited number of characteristics affecting the

energetic and economic efficiency of the individual steps, stages or cycles of a chemical manufacture and of the manufacture as a whole. The analysis of energetic and economic efficiency is valuable in that it gives the designer a chance to predict whether the new scheme will be economically attractive or not and to do so already at the earliest stage of the feasibility study. Through thermodynamic analysis, the designer is in a position to learn all that there is to know before he gets down to a detail design, thereby saving a good deal of time and effort.

Recently, there has been a growing interest in exergetic method of thermodynamic analysis. It is based on the concept of *exergy* and is applied to the study of industrial processes.

Highlights of the exergetic method. The rationale of the exergetic method is that any flows of energy-carrying media (water, steam, chemicals) or of energy (electricity or heat) are evaluated in terms of the maximum useful work that they are able to do.

Thus, *exergy* is the maximal capacity of a system to do work, subject to its interaction with the surroundings whose parameters are not affected by the system*.

The term 'surroundings' in the above definition refers to another system of a practically unlimited extent, characterized by constant-value properties — temperature T_0 , pressure p_0 , and chemical composition. The energy transferred to the surroundings as heat or work becomes the internal energy of the surroundings. The surroundings serve as an energy accumulator so large that its variables of state (temperature and pressure) remain unaffected despite the energy it receives. Thus, the surroundings are a source of starting materials and a depositary of products; they possess a minimum of free energy and cannot therefore be a source of work. A system in thermodynamic equilibrium with the surroundings loses its capacity to do any useful work. If the state variables of a substance are comparable with those of the components of the surroundings, the practical applicability of the substance as an energy source is nil. Therefore, its state of thermodynamic equilibrium with the surroundings is taken as the datum (or zero) level in calculating the practical applicability of the substance as an energy source. The practical applicability of heat decreases with decreasing difference between the temperature of the heat source and the ambient temperature. Any external sources of mass and energy present in the surroundings (say, chemical raw materials, fuel) whose properties markedly differ from those of the surroundings are treated separately from the surroundings.

* The term 'exergy' was coined by Z. Rant in 1956 from the Greek 'erg' for 'work' and the prefix 'ex' meaning 'from without', 'out', 'out of'.

In the general form, the exergetic balance in power for a flow of a substance may be written as

$$\dot{E} = \dot{E}_k + \dot{E}_p + \Delta_0 \dot{E} + \dot{E}_{ch} + \dot{E}_n + \dots \quad (2.31)$$

where:

$$\begin{aligned} \dot{E}_k &= \text{kinetic exergy} \\ \dot{E}_p &= \text{potential exergy} \\ \Delta_0 \dot{E} &= \text{physical exergy} \\ \dot{E}_{ch} &= \text{chemical exergy} \\ \dot{E}_n &= \text{nuclear exergy} \end{aligned}$$

From the view-point of chemical engineering, the most important terms in Eq. (2.31) are physical and chemical exergies. Their sum is called heat exergy or thermal exergy $\dot{E}_t$:

$$\dot{E}_t = \Delta_0 \dot{E} + \dot{E}_{ch} \quad (2.32)$$

The physical exergy of a substance is given by

$$\Delta_0 \dot{E} = \Delta H - T_0 \Delta S \quad (2.33)$$

where:

ΔH = difference in enthalpy between the start and end of the process

ΔS = change in entropy on passing from the starting materials (reactants) to products at the ambient temperature

The chemical exergy of a substance is given by

$$\dot{E}_{ch} = \sum_{j=1}^n \Delta \mu_j n_j \quad (2.34)$$

When finding the exergy of a substance by Eq. (2.33), one needs to know the respective enthalpy and entropy. Their values can be found in reference sources or calculated by the following equations:

— specific enthalpy

$$i_1 - i_0 = \int_{T_0}^{T_1} c_p dT \quad (2.35)$$

— specific entropy

$$s_1 - s_0 = \int_{T_0}^{T_1} c_p dT / T \quad (2.36)$$

If the heat capacities averaged over the operating temperature intervals are known, Eqs. (2.35) and (2.36) reduce, respectively, to the following expressions:

$$i_1 - i_0 = c_p \int_{T_0}^{T_1} (T_1 - T_0) \quad (2.37)$$

$$s_1 - s_0 = c_p \int_{T_0}^{T_1} \ln(T_1/T_0) \quad (2.38)$$

If, in the course of a process, the participating substances pass from one state of aggregation to another, the equation for the specific entropy takes the form

$$s_1 - s_0 = \int_{T_0}^{T_1} (c_p dT/T) + \sum (q_j/T_j) \quad (2.39)$$

where:

q_j = heat received or given by the system from or to the outside during a phase transformation

T_j = temperature at which the phase transformation took place

It may be added that the enthalpy of the system will also change by the amount q_j .

Example 2.1 Determine the exergy of molten phosphate ($g = 1000$ kg) at $T_1 = 1720$ K. The fusion point of phosphate is $T_f = 1670$ K, the heat of fusion is $q = 400$ kJ kg⁻¹; the heat capacity of solid phosphate in the temperature range 293-1670 K is $c_p = 1.2$ kJ kg⁻¹ K⁻¹; the heat capacity of the melt in the temperature range 1670-1720 K is $c_p = 1.4$ kJ kg⁻¹ K⁻¹.

In accord with Eqs. (2.35) through (2.39), the exergy of phosphate is

$$\begin{aligned} \dot{E} &= ge = g[i_1 - i_0 - T_0(s_1 - s_0)] \\ &= g \left\{ \left[c_p \int_{T_0}^{T_f} (T_f - T_0) + q + c_p \int_{T_f}^{T_1} (T_1 - T_f) \right] \right. \\ &\quad \left. - T_0 \left[c_p \int_{T_0}^{T_f} \ln(T_f/T_0) + q/T_f + c_p \int_{T_f}^{T_1} \ln(T_1/T_f) \right] \right\} \\ &= 1000 \times \{ [1.2 \times (1670 - 293) + 400 + 1.4 \times (1720 - 1670)] \\ &\quad - 293 \times [1.2 \ln(1670/293) + 400/1670 + 1.4 \ln(1720/1670)] \} \\ &= 1000 \times (2122 - 293 \times 2.37) \\ &= 1.43 \times 10^6 \text{ kJ} \end{aligned}$$

The maximum useful work done when a reaction goes on at constant pressure is equal, as will be recalled, to the free energy change:

$$W_{\max,p} = \Delta G = \Delta H - T\Delta S \quad (2.40)$$

Although Eq. (2.40) is outwardly similar to Eq. (2.33), the maximum work defined as the free energy change is in principle different from the ex-

ergy difference, $\Delta \dot{E}$. The values of ΔG and $\Delta \dot{E}$ will be the same only in a special case when $T = T_0$ and $p = p_0$. When the temperature of the system, T , is replaced with that of the surroundings, T_0 , important differences can be noted between ΔG and $\Delta \dot{E}$.

(1) ΔG is equal to the maximum work only when T and p are the same at both the start and end of the process. In contrast, $\Delta \dot{E}$ is equal to the maximum work of any process, provided it proceeds as a reversible interaction with the surroundings.

(2) When determining the maximum work, ΔG takes care of only internal processes in the system while $\Delta \dot{E}$ covers all forms of energetic interactions outside the system.

Exergetic balance. Exergetic efficiency. Material and energy (heat) balances are always used when one wishes to evaluate the economics of a chemical manufacturing process.

Unfortunately, an energy balance takes into account only the quantitative energy relations that have a bearing on the throughput of an item of equipment or of a plant as a whole, the consumption of the heat-transfer medium, and the efficiency. It does not evaluate qualitatively heat sources differing in physical nature and potential. The gap left by the classical material and energy balances based on the laws of conservation and conversion of mass and energy is filled by the exergetic balance which draws on the first and second principles of thermodynamics.

In the general case, the exergetic balance in power has the form

$$\Sigma \dot{E}' = \Sigma \dot{E}'' + D \quad (2.41)$$

where:

$\Sigma \dot{E}'$ = exergy flows entering the system

$\Sigma \dot{E}''$ = exergy flows leaving the system

D = exergy losses

It is to be noted that there is a fundamental difference between 'energy losses' and 'exergy losses'. As will be recalled, energy cannot vanish, and energy losses mean no losses in general, but the losses suffered by a given system or losses with respect to some objective if some energy cannot be utilized because its form or properties are unsuitable. In contrast, exergy losses mean that it is lost, destroyed completely because of energy dissipation. Quite aptly, exergy losses are often symbolized as D (for *dissipation*).

The differences between energy and exergy can clearly be seen from a comparison of the energy and exergy balances plotted in Fig. 2.1.

The flows of energy E are plotted to scale in Fig. 2.1a, and the flows of exergy $\dot{E}$, in Fig. 2.1b. As an example it is shown that two energy flows, E_1' and E_2' , enter the system, and three energy flows, E_1'' , E_2'' and E_3'' , leave the system. Here, E_3'' represents losses if E_2' is a heat flow. In accord with

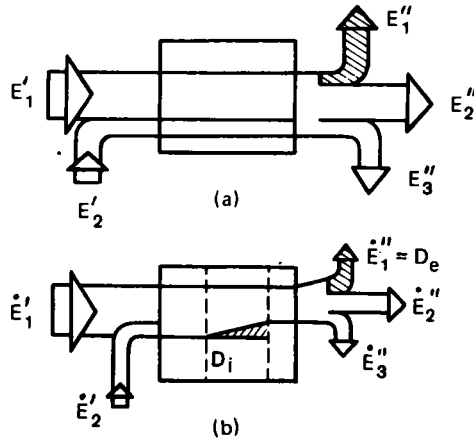


Fig. 2.1 Flow diagrams: (a) energy E and (b) exergy $\dot{E}$: E'_1, E'_2 and $\dot{E}'_1, \dot{E}'_2$ — at the inlet to the system; E''_1, E''_2, E''_3 and $\dot{E}''_1, \dot{E}''_2, \dot{E}''_3$ — at the outlet from the system; D_e and D_i — external and internal exergy losses

the law of conservation of energy,

$$E'_1 + E'_2 = E''_1 + E''_2 + E''_3$$

or, in the general case,

$$\Sigma E'_i = \Sigma E''_j$$

The energy efficiency is

$$\eta = \Sigma E''_u / \Sigma E' \quad (2.42)$$

where:

$\Sigma E''_u$ = sum of energies expended usefully

$\Sigma E'$ = sum of all inputs

In Fig. 2.1b, the incoming flows of exergy, $\dot{E}'_1$ and $\dot{E}'_2$, and the outgoing flows of exergy, $\dot{E}''_1$, $\dot{E}''_2$ and $\dot{E}''_3$, represent the capacity of energy to do work. The flows $\dot{E}'_1$ and E'_1 are drawn to have the same width in the diagram ($\dot{E}'_1 = E'_1$); this is the case when E'_1 is electric energy. Electric energy belongs to a class of energy forms that are transformable without limit, that is, are fully capable of doing work*. $\dot{E}'_2$ is shown smaller in size than E'_2 (here E'_2 is a heat flow). The value of $\Sigma \dot{E}''$ will always be smaller

* Constraints on the transformability of energy stem from the second principle of thermodynamics. In terms of transformability, energies may be classed into two forms (or kinds). Those falling in the first are fully transformable to any other forms; they cannot be characterized by entropy. These are electric, mechanical and other forms of energy. Those falling in the second are energies that cannot be completely transformed to other forms. Their transformability is decided both by the properties of the energy or the working fluid involved, and by the properties of the equilibrium surroundings. These forms of energy are characterized by a non-zero entropy. Energies falling in the second classification (the internal energy of a working fluid, chemical energy, energy transferred as a heat flow, etc.) consist each, as it were, of two parts: exergy and energy which cannot be converted to work (anergy). There is a well-defined relationship between anergy and entropy: Anergy is the energy of a completely disordered motion of molecules, and entropy is a measure of this disordered motion.

than that of $\Sigma \dot{E}'$ by the exergy losses D_i due to the irreversibility within the system

$$D_i = \Sigma \dot{E}' - \Sigma \dot{E}''$$

which fact is not reflected in the energy balance. There are also external exergy losses, D_e , associated with the exergy of nonusable outgoing flows, $\dot{E}''$.

The exergy losses due to irreversibility are found by the Gouy-Stodola equation:

$$D_i = T_0 \Delta S \quad (2.43)$$

where $\Delta \dot{S}$ is the change in the entropy of an isolated system.

The exergy losses caused by an irreversible heat transfer are plotted in the form of T -vs- S diagrams as shown in Fig. 2.2. The plot shows changes in the state of two flows which are in thermal contact with each other. The area A_{1256} represents the exergy of the flow which supplies heat and whose state changes along curve 1-2 ($\dot{E}_1 - \dot{E}_2$). The area A_{3475} represents the exergy of the flow which receives heat and whose state changes along curve 3-4 ($\dot{E}_4 - \dot{E}_3$).

The difference between the exergy received and given is the exergy losses due to the irreversibility of heat transfer:

$$D_i = (\dot{E}_1 - \dot{E}_2) - (\dot{E}_4 - \dot{E}_3) \quad (2.44)$$

Alternatively, these losses can be determined from the entropy of the heat-transfer agents and without invoking the exergies of the flows:

$$D_i = T_0 \Delta S = T_0 [(S_4 - S_3) - (S_1 - S_2)] \quad (2.45)$$

In Fig. 2.2, the exergy losses are shown as the shaded area.

The general law of conservation does not apply to exergy: The sum of the exergies of all the components of a system decreases in the course of a

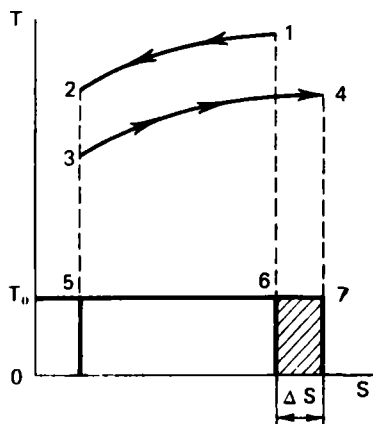


Fig. 2.2 Determining exergy losses from a T - S diagram

process. It is only when losses are nil (the process is reversible) that the sum of the exergies remains the same before and after a process. In each irreversible process, exergy is converted to energy. The ratio

$$\eta_e = \Sigma \dot{E}_u'' / \Sigma \dot{E}' = \frac{\Sigma \dot{E}' - (D_i + D_e)}{\Sigma \dot{E}'} < 1 \quad (2.46)$$

is the *exergetic efficiency* which is always less than unity. The exergetic efficiency of a system shows how closely the system approaches an ideal one. For an ideal process where the exergy losses D are nonexistent, $\eta_e = 1$, or 100%. If exergy received is completely lost in the course of a process, $\eta_e = 0$.

All real processes are irreversible, and their exergy losses increase and the work done by a system decreases with increasing entropy change in their course. Exergy losses are nonrecoverable losses of energy. It is the principal objective for the thermodynamic analysis of chemical engineering systems to determine why these losses occur and how large they are.

From his knowledge of the exergetic efficiency thus found, the designer can:

(a) objectively compare several versions of the same process or several processes intended to achieve the same goal and choose the one most effective in a given set of conditions from the view-point of exergy;

(b) determine from the absolute value of η_e if the process in question needs improvements;

(c) evaluate the relative influence of the various items of the energy balance on the efficiency of the process and choose ways and means of improving the performance of the process.

Thus, exergetic analysis reveals how perfect a process is thermodynamically, pin-points the principal sources of exergy losses, suggests how these losses could be minimized, and guides the designer towards a better technology.

At this writing, a wealth of experience has been accumulated in the use of exergetic analysis in chemical engineering. The literature is abundant with exergetic findings related to the manufacture of many products (methanol, nitric acid, and ammonia, to name but a few). A very instructive example is the exergetic analysis of an ammonia synthesis unit. Thus, as follows from an enthalpy balance, the losses of energy in the ammonia synthesis reactor (or the ammonia converter), water heater and heat exchangers are close to zero. The exergetic balance tells us quite the opposite — the exergy losses are especially heavy exactly in the ammonia converter: 22.6% of the total losses, which is greater than in the turbine (20%) and in the compressor (16%). The total losses in the ammonia converter, water heater, and heat exchangers account for nearly half of all the

exergy losses. Exergetic analysis shows that the losses could be reduced by as much as 15-18% without major changes in the process. The most impressive source of energy savings lies in radical changes in the process variables of ammonia synthesis (this may, for example, be a rise in temperature in one of the zones) — the heat of reaction could then be utilized to a better advantage and co-generation steam could be sold at a higher pressure and a higher temperature.

Recently, exergetic analysis has increasingly more been used in tackling technical and economic tasks in which process optimization includes both thermodynamic and economic estimation.

Chapter Three

USE OF CHEMICAL KINETICS IN THE CHOICE OF PROCESS VARIABLES

Chemical thermodynamics, as we have learned, tells us whether a reaction can occur by itself, without outside help. It also tells us what the position of equilibrium will be when the composition of the reaction mixture ceases to change. However, it cannot answer questions of important practical significance to chemical engineering: How fast will the reaction reach completion? How much time will it take to obtain a specified quantity of the reaction product?

Matters related to the speeds at which chemical changes take place — matters of primary importance when choosing the conditions for a chemical process to occur — are dealt with by *chemical kinetics*.

The objective of importance to chemical engineering is the final result of kinetic studies, that is, the form of the equation by which the rate of a chemical reaction can be computed under various conditions. Rate equations containing crucial information about the key mechanisms of chemical changes provide a basis on which to build a mathematical model of a chemical reactor. Without knowledge of kinetic relations, one could hardly be able to choose the reactor type judiciously and to calculate the reactor geometry.

The study of chemical kinetics, including the choice of kinetic variables, is the subject-matter of books on physical chemistry and chemical kinetics. This chapter will mainly be concerned with the practical applications of what is established by chemical kinetics.

3.1 The Rate of Homogeneous Chemical Reactions

The reaction rate, w_{rj} , is customarily expressed as the ratio between the quantity (number of moles n_j) of one of the reactants or products, J ,

reacted or produced per unit time τ per unit of the reaction space *. For a homogeneous chemical reaction,

$$w_{rJ} = \pm (1/V)(dn_J/d\tau) \quad (3.1)$$

where V is the reaction volume.

The reaction rate can be measured with respect to any participant in the reaction. It is always positive, therefore the sign preceding the derivative $dn_J/d\tau$ should be chosen according as species J is a reactant (in which case $dn_J/d\tau$ will be negative) or a product (in which case $dn_J/d\tau$ will be positive). Sometimes, there is no way of telling definitively whether species J is a reactant or a product. For example, in the series reactions

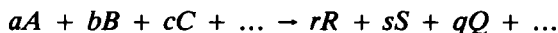


species R is the product for the first step and a reactant in the second. In such cases, the sign of the derivative is chosen according to the signs in the rate equation (see Sec. 2.2).

When a reaction takes place at a constant volume, the reaction rate is determined as the change in the molar concentration C_J per unit time:

$$w_{rJ} = \pm [d(n_J/V)]/d\tau = \pm dC_J/d\tau \quad (3.2)$$

When a chemical reaction is described by the stoichiometric equation



the changes in the quantity of reactants and products, Δn_J , caused by the reaction are connected by a relation of the form:

$$|\Delta n_A|/a = |\Delta n_B|/b = |\Delta n_C|/c = |\Delta n_R|/r = \dots = |\Delta n_J|/j \quad (3.3)$$

The reaction rates found from changes in the quantities of different reactants by Eq. (3.1) or Eq. (3.2) are different in magnitude if the stoichiometric coefficients of the reactants are not the same. On the other hand, it follows from Eqs. (3.1) and (3.3) that the reaction rates found from changes in the quantities of different reactants or products will satisfy the following condition:

$$w_{rA}/a = w_{rB}/b = w_{rC}/c = \dots = w_{rJ}/j \quad (3.4)$$

This situation leads to inconveniences in the quantitative determination of reaction rates, because the rate of one and the same reaction, as found

* In the case of homogeneous reactions, the term 'reaction space' refers to the reactor volume. In the case of heterogeneous reactions it is the surface area of the interface at which the process takes place. In the case of heterogeneous catalytic reactions it is the surface area of the interface or the quantity of the catalyst.

from changes in the quantities of different reactants, will be different numerically. To avoid this, we will, in our subsequent discussion, determine the reaction rate by the following equation:

$$w_{rJ} = \pm (1/j)(1/V)(dn_J/d\tau) = \pm (1/j)(dC_J/d\tau) \quad (3.5)$$

where j is the stoichiometric coefficient of species J with respect to which the reaction rate is found. In this way, the reaction rate is reduced to the common denominator and it will have the same numerical value, no matter which of the reactants or products is involved, that is:

$$w_{rA} = w_{rB} = \dots = w_{rJ} = w_r \quad (3.6)$$

Experimentally, the reaction rate is found by observing changes in the quantity (or concentration) of some reactant or product with time. Numerically, reaction rates are expressed in units of concentration per unit of time, for example, $\text{kmol m}^{-3} \text{h}^{-1}$ or $\text{mol litre}^{-1} \text{s}^{-1}$, etc.

3.2 The Reaction Rate as a Function of Reactant Concentration. Rate Equations

The rate of chemical reaction is a function of a quite a number of variables. As experimental studies of various reactions have shown, the reaction rate is affected not only by factors governing the state of chemical equilibrium (temperature, pressure, the composition of the reaction mixture), but also by some other causes, such as the presence or otherwise of extraneous substances that remain unchanged upon reaction, the conditions in which the reactants are physically transported to reaction sites, and the like.

The factors affecting the rate of a chemical transformation may be divided into two general groups: purely kinetic (or microkinetic) factors which determine the interaction rate at the molecular level, and macrokinetic factors which are responsible for the effect of the conditions in which the reactants are transported to the reaction zone, the presence or absence of mixing, and reactor geometry.

To begin with, we will discuss the effect of microkinetic factors on reaction rates.

The laws of chemical kinetics are based on two simple principles first established when studying reactions in solution:

The rate of a homogeneous reaction is proportional to the concentrations of the reactants.

The overall rate of several consecutive transformations widely differing in rate is determined by that of the slowest stage.

The functional relationship between the reaction rate and the concen-

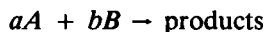
trations of the reaction-mixture constituents

$$w_r = w_r(C_A, C_B, \dots, C_J) \quad (3.7)$$

is referred to as the *rate equation* (or *rate law*) of reaction.

It is customary in chemical kinetics to class all reactions into *elementary* (or *simple*) and *nonelementary* (or *complex*) reactions.

An elementary (or single-step) reaction is that during which only one energy barrier has to be overcome as the reaction mixture passes from one state to another. The mechanism of an elementary reaction corresponds to its stoichiometric equation. The rate equation of, or the rate law for, the irreversible elementary reaction



has, in accord with the mass action law, the following form:

$$w_r = kC_A^a C_B^b \quad (3.8)$$

where k is referred to as the *rate constant* of the chemical reaction. The integer exponents a and b of the concentrations of reactants A and B in Eq. (3.8) for an elementary reaction are each called the *individual order* of the reaction with respect to the corresponding reactant. The sum of the individual orders

$$a + b = n$$

is called the *overall order* of the reaction. For elementary reactions, the individual orders (that is, the orders with respect to the reactants taken individually) are equal to the corresponding stoichiometric coefficients in the reaction equation.

Apart from the concept of 'reaction order', chemical kinetics also uses the concept of '*reaction molecularity*'. It is defined as the minimum number of molecules taking part in one single elementary step of the reaction at a time.

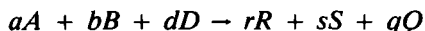
For elementary reactions, their order is equal to their molecularity, and it usually takes on values 1, 2, or 3. The order (or molecularity) of elementary reactions does not exceed value 3 because the probability of collision between more than 3 molecules at the same time is highly tenuous. Most elementary reactions are second-order reactions.

For the most part, however, chemical reactions are other than elementary: they take place via a number of intermediate steps. The stoichiometric equation of a non-elementary (multi-step) reaction reflects only the initial and final states of the reaction system involved and fails to describe the mechanism of the reaction in detail.

Sometimes it is convenient to treat a complex reaction as a *formally elementary one*, that is, as that which takes place in a single rather than

several steps. This is a legitimate simplification when, under the specified conditions, no intermediates are observed.

For the formally simple reaction



the rate equation (or the rate law) may, by analogy with a true simple (or elementary) reaction, be written as

$$w_{rA} = kC_A^\alpha C_B^\beta C_D^\delta$$

where the individual reaction orders α , β , and δ are found by experiment. In the general case, $\alpha \neq a$, $\beta \neq b$, and $\delta \neq d$. This means that the molecularity of the reaction is not the same as its order. The overall reaction order, $n = \alpha + \beta + \delta$, and the individual orders in such an equation may be integers, but they may likewise be fractional. This is because the mass action law that calls for the exponents of the concentrations in the rate equation to be only integers, is applicable solely to elementary reactions.

In addition to nonelementary reactions that may be regarded as formally simple ones, there are many nonelementary reactions which obviously break down into well-defined steps or stages (each stage yielding products in sizeable quantities).

The most common examples of nonelementary reactions are *concurrent* (or *parallel*) and *consecutive* (or *series*) reactions.

In parallel reactions, the same reactants may follow any one of several reaction pathways or routes, each yielding a product (or products) of its own. An example is the parallel reactions of ammonia oxidation, whose products may be either nitrogen (II) oxide, NO, or nitrogen (I) oxide, N₂O, or nitrogen, N₂.

In series reactions, the product of the first reaction is a reactant (or a starting material) for the second. In fact, a series reaction may consist of two or more steps following one after another. One example is the reaction in which a long-chained hydrocarbon is cleaved into progressively shorter molecules.

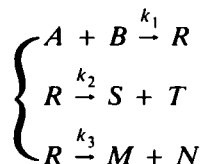
When the mechanism by which a complex reaction proceeds (that is, the elementary stages via which it takes place) is known, the following may be stated:

The reaction rate with respect to one of the participants is equal to the algebraic sum of the rates of the elementary stages in which this species takes part.

When deciding on the sign that should be given to the terms of this sum, it is convenient to use the following formal rules: (1) The time derivative of the concentration of the species involved, $dC_J/d\tau$, should be given the ' - ' sign, irrespective of whether species J is a reactant or a product. (2) The

rates of the elementary stages in which species J is used up (that is, species J is a reactant) are written in the total sum with a '+' sign; the rates of the stages in which species J is formed (it is a product) are written with a '-' sign.

Example 3.1 We set out to write the rate law with respect to species R and A which are participants in the complex (nonelementary) reaction



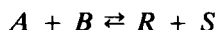
This reaction is seen to consist of three steps. The second and third steps are consecutive with respect to the first stage and concurrent (or parallel) with respect to each other. The rate with respect to species R which takes part in all the three steps is given by

$$w_{rR} = -dC_R/d\tau = -k_1 C_A C_B + k_2 C_R + k_3 C_R$$

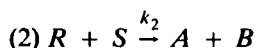
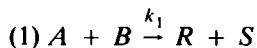
The rate with respect to reactant A which takes part in only the first elementary reaction is given by

$$w_{rA} = -dC_A/d\tau = k_1 C_A C_B$$

Example 3.2 From the view-point of chemical kinetics, the reversible reaction



may be regarded as a nonelementary reaction consisting of two steps:



Therefore, the rate at which the participants in this reaction disappear or are formed may be described by the following equations:

$$w_{rA} = -dC_A/d\tau = w_{rB} = -dC_B/d\tau = k_1 C_A C_B - k_2 C_R C_S$$

$$w_{rR} = -dC_R/d\tau = w_{rS} = -dC_S/d\tau = -k_1 C_A C_B + k_2 C_R C_S$$

3.3 Measurement of Reaction Rates of Simple and Complex Reactions

As has been noted, the reaction rate is a function of many variables. What follows from rate equations in the first place is that the rate of a sim-

ple reaction is proportional to the concentrations of the reactants. In consequence, an increase in the concentration of the reactants in simple reactions will practically always lead to an increase in the reaction rate (except the zero-order reactions where the rate is independent of concentration).

In complex reactions, one cannot say in advance if an increase in the concentration of a species can increase the reaction rate or the opposite may happen. As an example, we will consider a system of two concurrent (parallel) constant-temperature reactions differing in reaction order



Before one does anything to speed up the above overall reaction, it is important first to decide which of the two individual reactions is more important, that is, which reaction will yield the product one wishes to have. Most often, the chemical engineer is interested not in how fast reactant A is used up, but in how fast the desired end product is formed in comparison with by-products.

Let, in our example, R be the desired product and S , a by-product.

When analysing the relationship between the rates of the main and side reactions, resort is made to the point or differential selectivity, Eq. (1.26).

Let us, for convenience, re-write the stoichiometric equations of reaction (I) as



The rate at which reactant A is used up in the reaction yielding the desired product is numerically equal to the rate at which this product R is formed:

$$|w_{r(A-R)}| = |w_{rR}|$$

Recalling Eq. (3.5), we may write

$$\begin{aligned} |-dC_A/d\tau|_{A-R} &= \left| -\frac{1}{r/a_1} \frac{dC_R}{d\tau} \right| \\ &= \frac{1}{r/a_1} \frac{dC_R}{d\tau} \\ &= \frac{1}{\psi_{AR}} \frac{dC_R}{d\tau} \end{aligned} \quad (3.9)$$

where ψ_{AR} is the normalizing factor taking care of the stoichiometry of the reaction. When considering the above equation, it is important to

remember that $dC_R/d\tau > 0$ because R is the product and its concentration increases as the reaction goes on.

The overall rate at which reactant A is used up in concurrent (parallel) reactions (II) is equal to the sum of their individual rates:

$$w_{rA} = -dC_A/d\tau = \frac{1}{\psi_{AR}} \frac{dC_R}{d\tau} + \frac{1}{\psi_{AS}} \frac{dC_S}{d\tau} \quad (3.10)$$

Equation (1.26) which defines the differential selectivity may be re-written as

$$\varphi' = \frac{(1/\psi_{AR})(dC_R/d\tau)}{-(dC_A/d\tau)} = \frac{(1/\psi_{AR})(dC_R/d\tau)}{(1/\psi_{AR})(dC_R/d\tau) + (1/\psi_{AS})(dC_S/d\tau)} \quad (3.11)$$

In the general case, the differential selectivity does not remain unchanged as the process goes on because it is determined by the ratio of reaction rates, and the reaction rate does vary as the reaction goes on. Thus, the differential selectivity describes the effectiveness of the reaction that yields the desired product at some instant at some concentrations of the reactants and products and at some specified temperature. It remains constant only when the process variables remain unchanged with time (which may only happen when a process is carried out in a continuous well-stirred reactor under steady-state conditions).

As a reaction goes on, the concentrations of its reactants and products change. Let us see how the differential selectivity, φ' , varies with changes in the concentration of reactant A in the system of parallel reactions (II) at constant temperature.

Let the order of the reaction that yields the desired product be n_1 with respect to reactant A , and that of the side reaction, n_2 . Then,

$$w_{r(A \rightarrow R)} = k_1 C_A^{n_1} \quad (3.12)$$

$$w_{rA} = k_1 C_A^{n_1} + k_2 C_A^{n_2} \quad (3.13)$$

$$\varphi' = k_1 C_A^{n_1} / (k_1 C_A^{n_1} + k_2 C_A^{n_2}) \quad (3.14)$$

Let us analyse how φ' depends on the concentration of reactant A . For convenience, Eq. (3.14) may be re-cast as

$$\varphi' = \frac{1}{1 + (k_2/k_1) C_A^{n_2-n_1}} = 1/(1 + \lambda C_A^{\Delta n}) \quad (3.15)$$

where:

$\lambda = k_2/k_1$ = quantity independent of the concentration of reactant A

$\Delta n = n_2 - n_1$ = difference in order between the side and main reactions with respect to reactant A

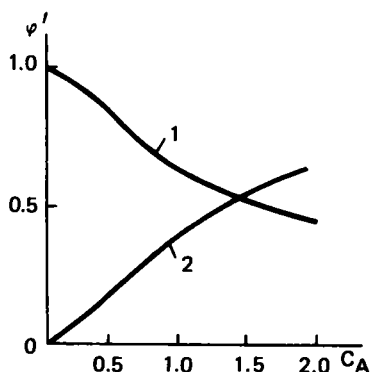


Fig. 3.1 Differential selectivity as a function of reactant *A* concentration for parallel reactions at reaction orders, n_1 and n_2 :

1, $n_1 = 1$, $k_1 = 10 \text{ hr}^{-1}$; $n_2 = 2.5$, $k_2 = 15 \text{ m}^{4.5} \text{ kmol}^{-1.5} \text{ hr}^{-1}$;
 2, $n_1 = 2.5$, $k_1 = 15 \text{ m}^{4.5} \text{ kmol}^{-1.5} \text{ hr}^{-1}$;
 $n_2 = 1$, $k_2 = 10 \text{ hr}^{-1}$

Obviously, φ' may be an increasing and a decreasing function of concentration. Let us determine how the function $\varphi'(C_A)$ varies by considering the sign of the first derivative:

$$d\varphi'/dC_A = -\Delta n \lambda C_A^{\Delta n - 1} / (1 + \lambda C_A^{\Delta n})^2 \quad (3.16)$$

As is seen from Eq. (3.16), the sign of the first derivative depends on the sign of Δn ($\lambda = k_2/k_1$ is always positive, C_A raised to any power is likewise positive). If $\Delta n < 0$, that is, if $n_1 > n_2$ (the order of the desired reaction with respect to the reactant is greater than that of the side reaction), then $\varphi'(C_A)$ is an increasing function: The rate of the reaction that yields the desired product increases with increasing concentration of the reactant faster than that of the side reaction and its contribution to the overall reaction rate increases (curve 2 in Fig. 3.1). In this case, the desired objective — an increased rate of formation for the desired product *R* in comparison with the rate of formation of the by-product *S* (an increase in the differential selectivity, φ') — is achieved through the use of the reactant in a high concentration.

At $\Delta n > 0$ ($n_1 < n_2$), the manner in which φ' depends on the reactant concentration is opposite to that obtaining in the previous case: $d\varphi'/dC_A < 0$ and, in consequence, $\varphi'(C_A)$ is a decreasing function (curve 1 in Fig. 3.1). In this case a higher differential selectivity with respect to the desired product is achieved at a lower concentration of the reactant.

Thus, it is not always advantageous to raise the concentration of the reactant. It should be added, though, that at low reactant concentrations and with all other conditions being equal, the absolute reaction rate will be low. In the circumstances, one ought to look for other ways and means of increasing the reaction rate while retaining a high differential selectivity.

When $\Delta n = 0$, the differential selectivity is, as is seen from Eq. (3.16), constant at any concentration of the reactants, and its value can only be changed by changing the ratio k_2/k_1 .

The simplest way to change this ratio is by changing the temperature of the reaction because temperature is among the process variables that affect the reaction rate most of all. Let us take a closer look at how temperature affects the reaction rate.

Experimental studies into the kinetics of chemical reactions have revealed that an increase of 10 deg in temperature brings about a two-fold to four-fold increase in reaction rate. More rigorously, this relation is expressed by what is known as the *Arrhenius equation*, after its discoverer, the Swedish chemist Svante Arrhenius:

$$k = k_0 \exp (-E/RT) \quad (3.17)$$

where:

k = rate constant

R = universal gas constant

T = absolute temperature

k_0 = frequency or pre-exponential factor

E = activation energy of the reaction

The activation energy of an elementary reaction, E , is the minimum excess energy above the average internal energy of the molecules, required for a chemical change to take place (or the energy barrier that the molecules must overcome when the reaction system passes from one state to another) *.

For reversible reactions the difference in activation energy between the forward reaction (E_1) and the backward reaction (E_2) is equal to the heat received or given by the reaction.

The frequency or pre-exponential factor k_0 is a proportionality constant whose magnitude is related to the collision frequency, the probability of the activated complex breaking down into the reactants without forming any products, molecular orientations during a collision, and some other factors affecting the reaction rate but independent of temperature. In a more rigorous treatment, it is important to remember that k_0 is likewise a function of temperature. At temperatures such that $RT \ll E$, however, this dependence may safely be ignored **.

As often as not, the Arrhenius equation is written for ease of analysis in a form where the logarithm of the rate constant is a function of the inverse temperature

$$\ln k = f(1/T)$$

* Some authors define the activation energy as a minimum kinetic energy that the molecules must possess jointly to overcome the repulsion between their electron clouds when they collide. This kinetic energy, which is changed to potential energy at the moment of impact, is the activation energy. — *Translator's note*.

** For most chemical-engineering processes, $E = 80$ at 100 kJ mol^{-1} . Thus, at a temperature of 300 to 1000K, ordinarily maintained during chemical reactions, the product RT describing the thermal energy of molecules is 1/20th to 1/70th of E .

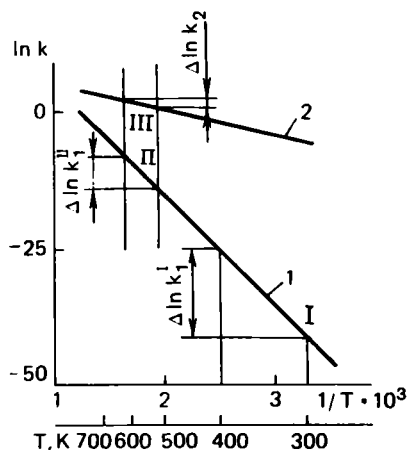


Fig. 3.2 Rate constant vs. temperature for chemical reactions with activation energies (1) 165 kJ mol^{-1} and (2) 40 kJ mol^{-1} :

region I: change in $\ln k$ with temperature raised from 300 to 400 K

region II: same, with temperature raised from 500 to 600 K

region III: same, for a reaction with a low activation energy, with temperature raised from 500 to 600 K

A plot of k as a function of $1/T$ is shown in Fig. 3.2. From its analysis, the following conclusions may be drawn.

Firstly, it follows from the nonuniform temperature scale laid off along the axis of abscissa that chemical reactions are most sensitive to temperature variations at low values of temperature. Straight line 1 corresponding to a chemical reaction with an activation energy of 165 kJ mol^{-1} shows two regions, I and II, where the temperature is changed by the same amount ($\Delta T = 100$ kelvins), but the two regions belong each to a different temperature range: region I falls within the temperature range close to room temperature; region II falls within the range of higher temperatures (around 300°C). When the temperature in region I is raised by 100°C , the rate constant k_1 increases by a factor of 1.9×10^7 . In contrast, when the same change in temperature takes place within region II, the rate constant k_2 increases only by a factor of 820 which is by about four orders of magnitude smaller than it is within region I. }

Secondly, as follows from comparison of the temperature dependence of rates for reactions with different values of activation energy, the latter shows a greater sensitivity towards temperature variations as it grows in magnitude. Straight line 1 in Fig. 3.2 applies to a reaction with an activation energy of 165 kJ mol^{-1} , and straight line 2, to a reaction with an activation energy of 40 kJ mol^{-1} .

As the temperature is raised from 500 to 600K, the rate of the first reaction (for which $E = 165 \text{ kJ mol}^{-1}$) increases by a factor of 820 (region II), and that of the second (with an activation energy $E = 40 \text{ kJ mol}^{-1}$), by a factor of only 5.3 (region III). This finding is of special importance when picking the process variables for complex (concurrent and consecutive) reactions. As an example, let us see how temperature affects the differen-

tial selectivity of concurrent (parallel) reactions (II):

$$\varphi' = 1/[1 + (k_2/k_1)C_A^{n_2-n_1}]$$

In order to observe the effect of only temperature on selectivity, suppose that the main and side reactions are of the same order ($n_1 = n_2$). Invoking Eq. (3.17), we may re-write Eq. (3.15) as follows:

$$\varphi = \frac{1}{1 + \frac{k_{2,0} \exp(-E_2/RT)}{k_{1,0} \exp(-E_1/RT)}} = 1/[1 + \sigma \exp(\Delta E/RT)] \quad (3.18)$$

On neglecting the effect of temperature on the frequency factors in the Arrhenius equation, we may conclude that $\sigma = k_{2,0}/k_{1,0}$ is independent of temperature as well. The derivative

$$d\varphi'/dT = \frac{(\Delta E/RT^2)\sigma \exp(\Delta E/RT)}{[1 + \sigma \exp(\Delta E/RT)]^2} \quad (3.19)$$

takes a '+' sign if $\Delta E = E_1 - E_2 > 0$ and a '-' sign if $\Delta E < 0$.

Thus, if the activation energy of the main reaction exceeds that of the side reaction, an increase in temperature will cause the differential selectivity to increase — this means that the rate of the main reaction will increase faster in comparison with that of the side reaction and with the overall rate of the process. Conversely, if $E_1 < E_2$, the temperature should be lowered rather than raised if we wish to increase the differential selectivity, φ' .

It is seen from the Arrhenius equation that one more route may, at least in principle, be used to control the reaction rate — by varying the magnitude of the activation energy E of the reaction. The height of the energy barrier involved in a reaction is closely related to the mechanism by which this reaction proceeds. If we change the pathway of a reaction by causing it to produce the desired products via some new intermediates, we will be able to control the activation energy as well. This approach is feasible when a catalyst is employed.

From what we have learned with regard to the effect of temperature on the rate of reactions differing in activation energy it follows that when a catalyst is used in order to speed up the main reaction in the case of concurrent (parallel) reactions, it may so happen that the activation energy of the side reaction is greater than that of the main reaction. Then an increase in temperature, often resorted to so as to accelerate a chemical process, will lead to a decrease in the selectivity with respect to the desired product.

Chapter Four

HETEROGENEOUS PROCESSES

Most reactions utilized in the chemical process industries involve substances which exist in different phases. Accordingly, there may be two-phase (or binary) and three-phase (or ternary) systems. For all the differences between them, they have one thing in common: Before a chemical reaction can take place, the reactants must be transported from the bulk of the stream carrying one phase to the interphase boundary or into the bulk of the other phase.

In homogeneous reactions, notably liquid-phase reactions, the diffusion of a material from one point of the reaction space to another also plays a role, especially in a large reactor. As a rule, however, the diffusion goes on so rapidly that it does not affect the reaction rate to a marked extent. In heterogeneous reactions, it is important to consider the rate at which the materials are transported from one phase to another because this transport does not proceed with ease. As often as not, the rate of a heterogeneous process may be decided by the rate of transport rather than by the reaction rate.

A distinction of any heterogeneous process is that it occurs in a number of stages — one or several purely chemical stages (that is, one or several chemical reactions) will always be accompanied by stages which may be called physical (in the sense that they do not involve any chemical transformations). These physical stages are associated with the transport of matter from one phase to the other, and the concentration of matter in the various phases (or in the bulk of a phase and at the interphase boundary) is different. The difference in concentration is the *driving force* for these transport processes (diffusion).

In the general case the rates of the various steps that make up a heterogeneous process may be substantially different and, say, temperature may differently affect both the reaction rate and the transport of matter from phase to phase.

If a complex process consists of parallel steps, its rate is the sum of the individual rates:

$$w_{\Sigma} = \sum_{i=1}^n w_i \quad (4.1)$$

If we take a process made up of several consecutive steps, we will see that the individual rates are related to the overall rate of the process differently, according as the process goes on under steady-state or unsteady-state conditions.

A process is said to go on under *steady-state conditions*, if at a given instant and at each point of the reaction space the properties of the system (say, the rate of the process, the composition of the reaction mixture, etc.) associated with a given point do not practically change. These properties are not necessarily the same at all points of the reaction space, but at each point they must remain invariant over all of the specified time interval.

Steady-state processes are typical of continuous flow (open) systems, although unsteady-state processes may likewise take place there (especially at the start-up). *Unsteady-state processes* are above all typical of closed systems. The rates of the consecutive steps that make up an unsteady-state process differ from one another, and the overall rate is equal to that of the slowest stage.

Under steady-state conditions, the rates of the individual consecutive steps 'adjust' themselves to that of the slowest step; they are all the same and equal to the overall rate of the process:

$$w_1 = w_2 = \dots = w_i = \dots = w_c \quad (4.2)$$

In various models, heterogeneous processes are treated as consisting of consecutive (series) or of consecutive and parallel (mixed) steps.

By definition (see Chap. 3), the rate of a heterogeneous chemical process is defined as the number of moles of one of the reactants or products that reacts or is formed per unit time per unit area of the interphase boundary. The rate of a heterogeneous process with respect to constituent J is given by

$$w_j = \pm (1/j)(1/S)(dn_j/d\tau) \quad (4.3)$$

where:

S = surface area over which the reaction takes place

j = stoichiometric coefficient of reactant (or product) J

So that the rates of the individual steps and of a heterogeneous process as a whole could be compared, they must all be expressed identically. In consequence, the rate of the chemical reaction step, w_{rj} , will be defined in accord with Eq. (4.3), and the rate of the diffusion step, w_{dj} , will likewise be defined as the quantity of species J transported per unit time across unit surface of the interphase boundary.

Sometimes, the rate of a heterogeneous chemical reaction is defined as the quantity of a species that reacts or is formed per unit time, that is, as $dn_j/d\tau$. This definition coincides with that of the throughput of a reactor (see Chap. 1). The throughput of a reactor increases with increasing size of the reaction space. In the case at hand, it is proportional to the area of the interface between the phases.

In describing the rate of a heterogeneous process, we will only use Eq. (4.3). Sometimes, this rate is called 'specific'. Obviously, thus defined, the rate is no longer dependent on the magnitude of the interfacial area.

Since the objective of any chemical process is to obtain a product as a result of a chemical transformation, the rate of a heterogeneous process cannot in any case exceed that of the chemical reaction involved. The point is that no matter how fast matter is transferred from one phase to the other, this transfer by itself cannot form the desired product.

On the other hand, the rate of a heterogeneous process cannot be greater than the rate of diffusion because the diffusion precedes the chemical reaction.

When analysing heterogeneous processes, two extreme, fundamentally different cases are considered. In the first case it may so happen that *the rate of the chemical reaction is high and exceeds the rate of the associated diffusion steps*. In the circumstances, the throughput of the reactor and the intensity of the process can be enhanced by removing the retarding effect of the diffusion steps. The heterogeneous process is then said to take place in the *diffusion region*.

In the second case *the rate of a chemical reaction under the specified operating conditions is small in comparison with the rate of the diffusion steps*. In the circumstances, the heterogeneous process as a whole can be promoted by adjusting the process variables so as to speed up the chemical reaction. The heterogeneous process is then said to take place in the *kinetic region*.

4.1 The Diffusion Steps of Heterogeneous Processes

As a heterogeneous reaction goes on, the concentrations of the reactants and products differ from one point of the reaction space to another. For example, when a gaseous reactant *A* reacts with a solid reactant *B*, the concentration of *A* at its surface will in the general case be lower than it is in the core of the gaseous stream that flows around the solid particles.

This difference in concentration gives rise to diffusion — a spontaneous process by which a substance is transferred as a result of a random motion of molecules from a region of high concentration to a region of low concentration until an equilibrium distribution is achieved. In this way, the random thermal motion of material species gives rise to an ordered, directional transport of the material within the regions where the above difference in concentration, or the *concentration gradient*, exists or between the regions where the concentration is other than an equilibrium one.

When considering heterogeneous processes, it is important to know the rate of the diffusion steps preceding the chemical reaction — May it not happen so that diffusion will impede chemical interactions?

The rate of diffusion is a function of the density and viscosity of the medium, temperature, the nature of the diffusing species, interactions of

external forces, etc. The relationships associated with diffusion are described by Fick's first and second laws.

In accord with *Fick's first law*, the quantity of constituent A transported by diffusion per unit time across a plane S of unit cross section, perpendicular to the direction of transfer, is proportional to the concentration gradient of the constituent at time τ :

$$-(1/S)(dn_A/d\tau) = D(\partial C_A/\partial z), \quad (4.4)$$

The symbol D represents the coefficient of molecular diffusion. Its dimensions are $[\text{Length}]^2 \times [\text{Time}]^{-1}$, for example, cm^2s^{-1} .

In the general case, concentration varies both in space and with time. Variations in the concentration of species A with time as a result of molecular diffusion is described by *Fick's second law*:

$$D(\partial^2 C_A/\partial z^2) = \partial C_A/\partial \tau \quad (4.5)$$

or, when diffusion takes place in a 3-dimensional space,

$$\partial C_A/\partial \tau = D\nabla^2 C_A = D(\partial^2 C_A/\partial x^2 + \partial^2 C_A/\partial y^2 + \partial^2 C_A/\partial z^2) \quad (4.6)$$

On replacing the concentration gradient with the ratio of finite changes in Eq. (4.4), we get

$$w_d = -(1/S)(dn_A/d\tau) = D(\partial C_A/\partial z) \approx D(\Delta C_A/\Delta z) \quad (4.7)$$

where:

ΔC_A = change in concentration over the distance $\Delta z = \delta$

$\Delta z = \delta$ = thickness of the layer through which the diffusion flux travels

Then,

$$w_d \approx \beta \Delta C_A \quad (4.8)$$

where

$$\beta = D/\Delta z = D/\delta \quad (4.9)$$

is a proportionality factor called the *individual mass transfer coefficient*. *

When a heterogeneous process takes place at the interface between phases, the reactants are used up and the products are formed. For the process to go on under steady-state conditions, it is essential that the reactants used up at the reaction surface be continuously replenished and the products be as continuously withdrawn from the interface. The necessary transport occurs owing to diffusion as long as there is a concentration gradient. A fast reaction calls for a fast diffusion — otherwise the chemical reaction will be retarded by diffusion processes.

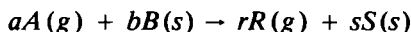
* Not to be confused with the overall mass transfer coefficient. — *Translator's note.*

It may be deemed that diffusion takes place in the layer lying just below the interface. Inside this diffusion layer, mass transfer is due solely to molecular diffusion. A decrease in the thickness, δ , of this layer leads, in accord with Eq. (4.9), to a greater individual mass transfer coefficient.

The coefficient of molecular diffusion D is a function of the molecular properties of the substance that diffuses and the substance in which the diffusion takes place. It only slightly rises with increasing temperature (in proportion to about $T^{3/2}$) and decreases with increasing pressure. Most often the *diffusion coefficient*, or *diffusivity*, is found by experiment or from empirical or semi-empirical relations.

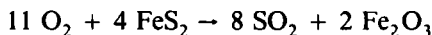
4.2 Heterogeneous Processes in a Gas-Solid System (Gas-Solid Reactions)

Heterogeneous processes in a gas-solid system are a very common occurrence in the chemical process industries. Notably, they are used in the roasting of ores, the preparation of cement clinker, the absorption of hydrogen sulphide by zinc oxide, etc. This group may be further divided into several forms of heterogeneous processes. The most common case is the heterogeneous reaction whose participants (reactants and products) may be gases and solids:

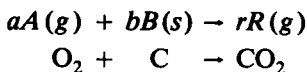


where the letter “g” in the parentheses stands for “gas” and the letter “s” in the parentheses, for “solid”.

This reaction, for example, takes place when iron pyrite is roasted:

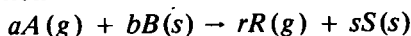


In some reactions, there may be either no gaseous reactant or no solid product, etc. For example,



4.2.1 Kinetic Models of Heterogeneous Processes in a Gas-Solid System

Quite a number of kinetic models have been developed, somewhat simplifying the nature of heterogeneous processes, but enabling them to be described with relatively simple equations. The most commonly used types are the *unreacted-core model* and the *quasi-homogeneous model*. What sets them apart from each other can be seen from a look at the heterogeneous reaction



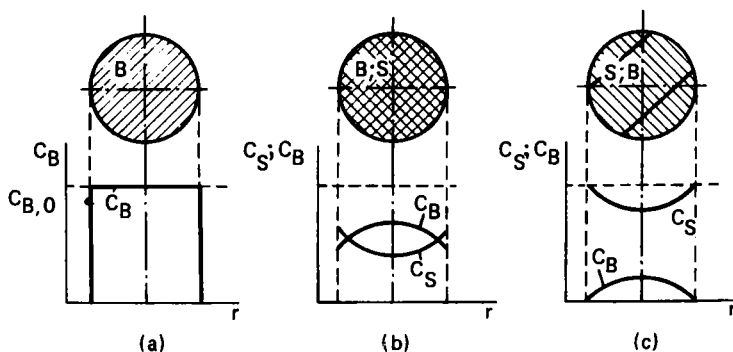


Fig. 4.1 Sketch of a solid particle during a heterogeneous process described by the quasi-homogeneous model:

a, prior to reaction; *b*, at an intermediate instant; *c*, nearly fully converted particle

in the course of which the external dimensions of a selected solid particle remain unchanged.

The quasi-homogeneous model assumes that the heterogeneous process goes on simultaneously at any point within the bulk of the solid particle. This can be so if the gaseous reactant is free to get inside the solid phase, that is, there is a multitude of pores in the solid particle, and the chemical reaction that takes place at the surface of these pores proceeds at a sufficiently slow rate. In diagrammatic form, Fig. 4.1 shows how the concentration of the solid reactant *B* changes throughout the bulk of the solid phase at different instants after the onset of the reaction, when the heterogeneous process answers the quasi-homogeneous model.

The unreacted-core model is more often used. It assumes that the chemical reaction first takes place at the outer surface of the solid particle and the deeper layers do not take part in the reaction until all of the outer layer has turned into solid or gaseous products. Gradually, the reaction zone moves inside, leaving behind a solid product and the inert constituent of the solid reactant (ash).

At any given instant, the solid particle consists of a core surrounded by an envelope. The core is the unreacted reactant (this is the reason why this model is referred to as the unreacted-core model). The envelope consists of a solid product and inert constituents. The manner in which a heterogeneous process develops in accord with this model is shown in Fig. 4.2.

Let us take a closer look at a heterogeneous process answering the unreacted-core model. We will examine a single solid particle whose external dimensions remain unchanged with time and which is passed over by the stream of the gaseous reactant *A*. The various stages of this process will

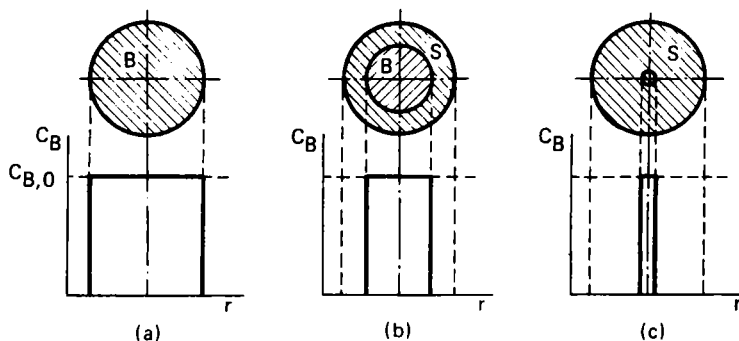


Fig. 4.2 Concentration profile of solid reactant B with progress of a heterogeneous process described by the unreacted-core model:

a , prior to reaction; b , at an intermediate instant; c , nearly fully converted particle

be assessed in terms of the concentration of reactant A at different points of the reaction space (Fig. 4.3).

Any heterogeneous process answering the unreacted-core model may be divided into five basic steps as follows.

1. Surface or external diffusion: Reactant A diffuses to the external surface of the solid particle from the bulk gas phase through a layer depleted of this constituent.

2. Pore or internal diffusion: The gaseous reactant finds its way through pores in the solid product to the core of the solid reactant.

3. A chemical reaction takes place at the surface of the unreacted core.

4. Pore or internal diffusion: The gaseous products diffuse through the layer of solid products.

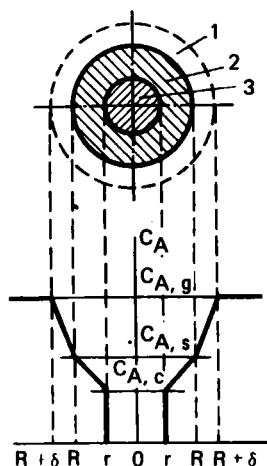


Fig. 4.3 Concentration profile of a gaseous reactant reacting with a solid particle (the unreacted-core model):

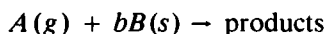
1, boundary gaseous film with a lower reactant A concentration than in the gas stream
2, solid reaction product layer (ash layer)
3, unreacted core of reactant B

5. Surface or external diffusion: The gaseous products diffuse into the bulk gas phase.

In some cases, steps 4 and 5 may be omitted, notably when the chemical reaction in question is an irreversible one.

4.2.2 The Basic Steps of a Process Answering the Unreacted-Core Model

Surface or external diffusion. As a result of the reaction



the concentration of the gaseous reactant A at the surface of the solid particle is lower than it is in the bulk gas phase. There is no way of exactly locating the boundary where the concentration of the gaseous reactant begins to fall — as the gas stream passes over the solid particle, the location of the boundary may vary. It may be agreed, however, that the boundary lies at some distance δ from the surface of the solid particle. Then we may arbitrarily presume the existence of a gaseous surface film of thickness δ , such that beyond it the concentration of the gas reactant is constant and equal to $C_{A,g}$ (where 'g' stands for 'gas'), while inside the film C_A decreases from $C_{A,g}$ to its value at the surface of the solid particle, $C_{A,s}$ (where 's' stands for 'surface').

Reactant A is transported from the bulk gas phase to the surface of the solid particle across the gaseous boundary film both by molecular diffusion (whose mechanism we have already discussed) and by its motion with the gas stream in the direction of the flow, that is, by convective transport. The overall transfer of the reactant is by molecular diffusion, and convective transport is called *convective diffusion*.

Convective diffusion may be described by the following differential equation:

$$\begin{aligned} -u_x(\partial C_A/\partial x) - u_y(\partial C_A/\partial y) - u_z(\partial C_A/\partial z) \\ + D(\partial^2 C_A/\partial x^2 + \partial^2 C_A/\partial y^2 + \partial^2 C_A/\partial z^2) = \partial C_A/\partial \tau \end{aligned} \quad (4.10)$$

or, in a more compact form,

$$-u \text{ grad } C_A + D \nabla^2 C_A = \partial C_A/\partial \tau \quad (4.11)$$

where u_x , u_y , and u_z are the linear velocities of the stream in the x -, y -, and z -direction, respectively.

Because the variables in Eq. (4.10) and (4.11) are both the concentration and linear velocity of the gaseous stream, this equation would have to be solved simultaneously with the differential equations of fluid dynamics. As a result, we would obtain a set of differential equations which has no analytical solution.

Ordinarily, the rate of convective diffusion is found by the equation

$$w_{conv} = -(1/S)(dn_A/d\tau) = \beta(C_{A,g} - C_{A,s}) \quad (4.12)$$

where:

w_{conv} = rate of convective diffusion, that is, the quantity of gaseous reactant A transported by convective diffusion per unit area per unit time

β = individual mass transfer coefficient which is a function of fluid dynamics of the stream

It is assumed that there is, at the surface of the solid particle, a stationary diffusion layer of thickness δ_1 , inside which mass transfer is solely by molecular diffusion. The rate of surface (convective) diffusion across a real gaseous film of thickness δ may then be equated to the rate of molecular diffusion through the diffusion layer of thickness δ_1 . In accord with Eq. (4.9), the individual mass transfer coefficient is

$$\beta = D/\delta_1$$

where D is the coefficient of molecular diffusion.

The rate of surface diffusion may be raised either by increasing the driving force which is equal to the difference between $C_{A,g}$ and $C_{A,s}$, or by increasing the individual mass transfer coefficient.

If we wish to increase β , we should (1) increase, if possible, the coefficient of diffusion D or (2) decrease the thickness of the gaseous film, δ_1 .

As has been shown, the coefficient of molecular diffusion is mainly decided by the molecular structure of the participants in the diffusion process and only slightly depends on temperature and pressure. For example, the increase in temperature from 700 to 800K causes the coefficient of molecular diffusion for reactants moving into a gaseous film to rise by a small factor of $(800/700)^{1.5} = 1.22$. Thus, the process temperature cannot serve as a reliable means of speeding up surface diffusion.

A more impressive result can be obtained by reducing the thickness δ_1 of the gaseous film. Although, within the framework of the adopted model, we cannot definitively say what the numerical value of δ_1 is, it is a safe guess, however, that any method of reducing the film thickness will serve to increase the individual mass transfer coefficient. These methods may be an increase in the linear velocity of the gaseous stream passing over the solid particle so that the particle is stripped off its film, and the agitation of the solid phase as in fluidized-bed reactors.

Pore or internal diffusion. When a heterogeneous reaction involving a gaseous reactant and a solid reactant yields solid products in addition to gaseous products, the step that will precede the chemical reaction proper and follow surface diffusion will be pore or internal diffusion — the move-

ment of the gaseous reactant through the layer of solid products towards the surface of the core where the chemical reaction takes place.

The rate of pore diffusion is given by

$$\begin{aligned} w_d &= -(1/S)(dn_A/d\tau) \\ &= D_{eff}(dC_A/dr) \end{aligned}$$

where D_{eff} is the effective diffusion coefficient which depends on the porosity of the solid, the tortuosity of pores, etc.

Because the layer of reaction products presents a definite resistance to the transport of reactant A from the gaseous boundary film to the core surface, its concentration will gradually decrease on moving towards the core surface from $C_{A,s}$ at the external surface of the solid particle to $C_{A,c}$ (where 'c' stands for 'core') at the core surface (see Fig. 4.3).

If the ash layer is not very thick, it may arbitrarily be deemed that

$$dC_A/dr \approx \Delta C_A/\Delta r = (C_{A,s} - C_{A,c})/(R - r) \quad (4.15)$$

where:

R = outer radius of the solid particle, assumed constant for a particle whose external dimensions remain unchanged

r = core radius which decreases as the process goes on

Then the rate of pore diffusion may be written as

$$\begin{aligned} w_d &= -(1/S)(dn_A/d\tau) \approx (D_{eff}/\Delta r)(C_{A,s} - C_{A,c}) \\ &= \beta'(C_{A,s} - C_{A,c}) \end{aligned} \quad (4.16)$$

As is seen, the equation describing the rate of pore diffusion is similar in its structure to the equation describing the rate of surface diffusion: it is the product of the difference in concentration by the individual mass transfer coefficient.

$$\beta' = D_{eff}/\Delta r$$

The rate of pore diffusion may largely be enhanced by increasing the individual mass transfer coefficient β' . However, a substantial increase in the diffusion coefficient, as has been demonstrated, is difficult to obtain. Therefore, the preferable approach should be a decrease in the thickness of the solid product layer, equal to $R - r$. The maximum thickness of this layer is R (at $r = 0$), that is, the outer radius of the solid particle. A decrease in the size of the solid particle (comminution) automatically leads to a decrease in the thickness of the solid product layer, that is, to an increased individual mass transfer coefficient, β' . Thus, the comminution of solids offers the utmost in speeding up pore diffusion.

The surface chemical reaction. The principal step of a heterogeneous chemical process is the surface reaction which brings about all the changes that constitute the heterogeneous process.

If the chemical reaction is an irreversible one (and this is a prevalent class of chemical reactions, exemplified by the combustion of solids), the concentration of the gaseous reactant at the core surface will decrease from $C_{A,c}$ achieved following the pore diffusion step, to zero, that is, to its complete exhaustion.

The surface reaction rate may be described by invoking the laws of chemical kinetics:

$$w_r = -(1/S)(dn_A/d\tau) = k_s C_{A,c}^n \quad (4.17)$$

where:

k_s = rate constant of the surface chemical reaction
 n = order of the reaction

When doing quantitative computations it is important to remember that the surface reaction rate is expressed as the quantity of matter used up per unit time per unit reaction surface area (for example, $\text{kmol m}^{-2} \text{hr}^{-1}$), and this affects the units in which k_s is expressed:

$$[k_s] = [w_r]/[C_{A,c}]^n$$

Taking a 1st-order reaction as an example,

$$[k_s] = \frac{\text{kmol m}^{-2} \text{hr}^{-1}}{\text{kmol m}^{-3}} = \text{m hr}^{-1}$$

which contrasts with the units used to express the rate of a bulk reaction, $[k] = \text{hr}^{-1}$.

As is with the preceding steps, the rate of the chemical reaction step may be enhanced either by an increase in the concentration of the gaseous reactant, $C_{A,c}$ (which can obviously be achieved by raising $C_{A,g}$, that is, the concentration of the gaseous reactant in the stream passing over the particle) or, primarily, by raising the rate constant of the chemical reaction, k_s . Since, in accord with Arrhenius' equation, the rate constant of a chemical reaction exponentially rises with increasing temperature, it follows that a heterogeneous process taking place in the kinetic region can best be speeded up by raising the temperature of the process.

4.2.3 The Rate Constant of a Heterogeneous Process. The Rate-Controlling Step of a Reaction

Using Eqs. (4.12), (4.16) and (4.17), we can readily find the rates of the individual steps of a heterogeneous process. However, these steps are inter-related rather than isolated from one another. Therefore, if we wish to find the overall rate of a heterogeneous process, we need an equation that would take into account the specifics of each step.

By analogy with the law of mass action, it would be convenient to express the rate of a heterogeneous process as the product of some rate cons-

tant, K , by the concentration of the gaseous reactant in the bulk gas phase, $C_{A,g}$:

$$w_A = KC_{A,g} \quad (4.18)$$

This is quite applicable when a heterogeneous process including a 1st-order reaction goes on under steady-state conditions. In the circumstances, one uses Eq. (4.2) which states that the consecutive steps of a steady-state process proceed all at the same rate.

Let us write the equations giving the rates of the individual steps:

$$w_{conv,A} = \beta(C_{A,g} - C_{A,s}) \quad (4.19)$$

$$\begin{aligned} w_{d,A} &= D(dC_A/dr) \approx (D/\Delta r)(C_{A,s} - C_{A,c}) \\ &= \beta'(C_{A,s} - C_{A,c}) \end{aligned} \quad (4.20)$$

$$w_{r,A} = k_s C_{A,c} \quad (4.21)$$

Let us re-cast Eqs. (4.19) through (4.21) in such a way that the concentrations of the reactants are on their right-hand sides, and add them together termwise, recalling that under steady-state conditions

$$w_{r,A} = w_{d,A} = w_{conv,A} = w_A$$

Then,

$$w_{conv,A}(1/\beta) = C_{A,g} - C_{A,s}$$

$$w_{d,A}(1/\beta') = C_{A,s} - C_{A,c}$$

$$w_{r,A}(1/k_s) = C_{A,c}$$

$$w_A(1/\beta + 1/\beta' + 1/k_s) = C_{A,g}$$

And finally,

$$w_A = \frac{1}{1/\beta + 1/\beta' + 1/k_s} C_{A,g} = KC_{A,g} \quad (4.22)$$

To sum up, the rate of a heterogeneous process is the product of its rate constant, K , by the concentration of reactant A in the gas phase, $C_{A,g}$.

Let us analyse the rate constant of a heterogeneous process, K . The denominator is the sum of the reciprocal rates of the individual steps. By analogy with the mass transfer coefficient used in the theory of mass transfer, this sum may be regarded as the sum of the resistances presented at the individual steps of a heterogeneous process.

Situations may arise where the resistance of one of the steps substantially exceeds that presented by the two other steps. Then, the rate constant of the heterogeneous process will, with a sufficiently good approximation, be equal to the individual mass transfer coefficient of the first step. For example, if

$$1/\beta \gg 1/\beta' \quad \text{and} \quad 1/\beta \gg 1/k_s$$

then,

$$K \approx \beta$$

and

$$w_A = KC_{A,g} \approx \beta C_{A,g} \quad (4.23)$$

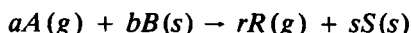
That is, the rate of the process is decided by the rate of the convective diffusion of reactant A through the gaseous boundary film.

Alternatively, Eq. (4.23) may be derived from Eq. (4.19) on setting $C_{A,s} = 0$. To prove, if the resistance due to surface diffusion markedly exceeds that due to pore diffusion, and the surface reaction goes on at a high rate, the concentration of reactant A practically observable at the surface of the solid particle, $C_{A,s}$, will be zero because all the molecules of reactant A , on overcoming the substantial surface-diffusion opposition, will meet no further resistance and will be able to pass through the solid-product layer and to take part in the reaction. Thus, this step is characterized by a maximum change in the concentration of the gaseous reactant.

When there is such a step, it is referred to as the *rate-controlling step* of a process because it determines the rate of the heterogeneous process as a whole.

4.2.4 Design Relationships between the Time of a Heterogeneous Reaction and the Conversion of the Solid Reactant

Suppose that a single solid particle of reactant B reacts with the stream of gaseous reactant A passing over it according to the scheme



Also suppose that the solid particle is a sphere and that its external dimensions remain unchanged during the reaction. Let the particle's radius be R , and the core radius, r .

In order to establish the relationship between x_B and τ , we need to know the rate of the process and the factors that govern it. If the rate of a heterogeneous process is controlled by one of its consecutive steps, the overall rate of the process will be equal to the rate of that step, and the derivation of the function $x_B(\tau)$ is simplified considerably.

We will consider cases where the rate of the process is controlled by surface diffusion, pore diffusion, and the chemical reaction.

The rate-controlling step is surface diffusion. In such a case, most of the resistance is presented when the gaseous reactant A passes through the gaseous boundary film depleted of that reactant. In the circumstances, the rate of the heterogeneous process is equal to the rate of convective diffusion and is given by

$$w_A = w_{\text{conv},A} = -(1/S)(dn_A/d\tau) = \beta(C_{A,g} - C_{A,s}) \quad (4.24)$$

Figure 4.4 shows the concentration profile of the gaseous reactant for a process going on in the surface-diffusion region. Since in this case the steps

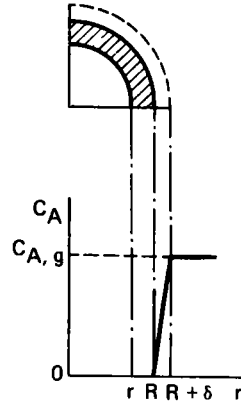


Fig. 4.4 Concentration profile of a gaseous reactant, with the rate of the heterogeneous process controlled by external diffusion

following the diffusion of reactant A through the gaseous boundary film do not present any opposition to the further diffusion of reactant A through the solid-product layer and its reaction with the core of reactant B , it may be assumed that the concentration of reactant A at the surface of the solid particle, $C_{A,s}$, is zero.

In view of this, Eq. (4.24) can be simplified as follows:

$$w_A = -(1/S)(dn_A/dr) = \beta C_{A,g} \quad (4.25)$$

The rate of a heterogeneous reaction may be expressed both in terms of changes in the quantity of gaseous reactant A with time, and in terms of changes in the quantity of solid reactant B

$$w_A = w_B = -(1/b)(1/S)(dn_B/dr) = \beta C_{A,g} \quad (4.26)$$

The quantity of reactant B in a solid particle may be expressed as the product of the core volume V_c by the molar density ρ_B (in fact, this is the molar concentration of reactant B in kmol m^{-3}):

$$n_B = V_B \rho_B$$

Since the solid particle has been assumed to be a sphere, it follows that

$$V_B = 4\pi r^3/3$$

Then,

$$dn_B = d(V_B \rho_B) = d(4\pi r^3 \rho_B/3) = 4\pi \rho_B r^2 dr \quad (4.27)$$

The area to which the rate of surface diffusion is referred is the external surface area of a solid particle whose radius is R :

$$S = 4\pi R^2 \quad (4.28)$$

On substituting for dn_B from Eq. (4.27) and for S from Eq. (4.28) into

Eq. (4.26), we get

$$-(1/b)(1/4 \pi R^2)4\pi\rho_B r^2(dr/d\tau) = \beta C_{A,g} \quad (4.29)$$

On solving the differential equation (4.29), we obtain

$$\int_0^\tau d\tau = -(\rho_B/b\beta C_{A,g} R^2) \int_R^r r^2 dr$$

Hence,

$$\begin{aligned} \tau &= (\rho_B/b\beta C_{A,g} R^2)(R^3/3 - r^3/3) \\ &= (\rho_B R^3/3b\beta C_{A,g} R^2)(1 - r^3/R^3) \end{aligned}$$

The ratio r^3/R^3 may be replaced with the ratio between the core volume and the total volume of the solid particle, ($V_B/V_0 = r^3/R^3$). Then, on multiplying the numerator and the denominator by ρ_B , we obtain

$$r^3/R^3 = V_B/V_0 = V_B\rho_B/V_0\rho_B = n_B/n_{B,0} = 1 - x_B \quad (4.30)$$

where V_0 is the volume of the solid particle.

In view of Eq. (4.30),

$$\tau = (\rho_B R/3b\beta C_{A,g})[1 - (1 - x_B)] = (\rho_B R/3b\beta C_{A,g})x_B \quad (4.31)$$

When $x_B = 1$ (which means that all of the reactant B has reacted), Eq. (4.31) makes it possible to find the time required for complete transformation of the solid particle, τ_{comp} , when the heterogeneous process is limited by surface diffusion:

$$\tau_{comp} = \rho_B R/3b\beta C_{A,g} \quad (4.32)$$

Thus, when a heterogeneous process goes on in the surface diffusion region, there is a linear relationship between τ and x_B :

$$\tau = \tau_{comp} x_B \quad (4.33)$$

When a heterogeneous reaction is effected in a commercial reactor, it is legitimate to regard each solid particle as a microreactor in its own right. One way to enhance the throughput of a reactor is to reduce the time required for complete conversion of the solid particle, τ_{comp} . When a heterogeneous process goes on in the surface diffusion region, this can be done by reducing the radius and increasing the concentration of the gaseous reactant, $C_{A,g}$, and also by increasing the individual mass transfer coefficient. The latter can be accomplished, as has been noted, by increasing the linear velocity of the gas stream and by making it turbulent.

The rate-controlling step is pore diffusion. When the rate of a heterogeneous process is controlled by pore diffusion, most of the resistance is presented at this step, and the concentration of the gaseous reactant changes from $C_{A,g}$ to zero on moving from the outer envelope to the core (Fig. 4.5).

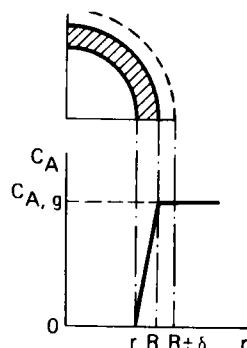


Fig. 4.5 Concentration profile of a gaseous reactant, with the rate of the heterogeneous process controlled by pore diffusion

In the circumstances, the rate of the heterogeneous process may be equated to the rate of diffusion through the porous layer of the solid products:

$$w_A = -(1/S)(dn_A/dr) = -(1/S)(1/b)(dn_B/dr) = D(dC_A/dr) \quad (4.34)$$

The area S to which the rate of a pore-diffusion limited heterogeneous process is referred is the surface area of the core of radius r . Given a spherical solid particle.

$$S = 4\pi r^2 \quad (4.35)$$

Proceeding from physical considerations, we may somewhat simplify the mathematics involved in solving Eq. (4.34) by assuming quasi-steady conditions for the diffusion of reactant A relative to the movement of the core boundary of reactant B towards the centre of the particle.

The diffusion of reactant A from the periphery of the particle towards the surface of the unreacted core is accompanied by the movement of the core boundary towards the centre of the particle.

At the first step of integration, suppose that the rate at which the dimensions of the core change (it is given by the derivative $dn_B/dr = \rho_B dV_B/dr$) is constant (quasi-steady) with respect to the rate of gas diffusion governed by the concentration gradient, dC_A/dr . Then, subject to Eq. (4.35), we may write Eq. (4.34) as

$$-(dn_B/dr) \int_R^r (dr/r^2) = 4\pi Db \int_{C_{A,s}=C_{A,g}}^{C_{A,c}=0} dC_A \quad (4.36)$$

Hence,

$$-(dn_B/dr)(1/r - 1/R) = 4\pi Db C_{A,g} \quad (4.37)$$

At the second step of integration, suppose that the dimensions of the core are changed. Since, in accord with Eq. (4.27), $dn_B = 4\pi r^2 \rho_B dr$, we

may re-cast Eq. (4.37) as

$$-4\pi r^2 \rho_B (dr/d\tau)(1/r - 1/R) = 4\pi D b C_{A,g} \quad (4.38)$$

Let us integrate Eq. (4.38) with respect to time between the limits $\tau = 0$ (when the core is equal in size to the whole solid particle, that is, $r = R$) and the current instant τ when the unreacted core has a radius r :

$$\begin{aligned} \int_0^\tau d\tau &= -(\rho_B/bDC_{A,g}) \left[\int_R^r r dr - (1/R) \int_R^r r^2 dr \right] \\ &= -(\rho_B/bDC_{A,g}) [(r^2/2 - R^2/2) - (1/R)(r^3/3 - R^3/3)] \quad (4.39) \end{aligned}$$

On reducing the fractions in the square brackets in Eq. (4.39) to a common denominator and taking R^3 out of the brackets, we get

$$\tau = (\rho_B R^2 / 6bDC_{A,g}) (1 - 3r^2/R^2 + 2r^3/R^3) \quad (4.40)$$

In view of Eq. (4.30),

$$\tau = (\rho_B R^2 / 6bDC_{A,g}) [1 - 3(1 - x_B)^{2/3} + 2(1 - x_B)] \quad (4.41)$$

At $x_B = 1$, we may use Eq. (4.41) to compute the time required for complete conversion of the solid particle, τ_{comp} , when the heterogeneous process goes on in the pore-diffusion region:

$$\tau_{comp} = \rho_B R^2 / 6bDC_{A,g} \quad (4.42)$$

To sum up, for an uncatalyzed heterogeneous process taking place in the pore-diffusion region

$$\tau = \tau_{comp} [1 - 3(1 - x_B)^{2/3} + 2(1 - x_B)] \quad (4.43)$$

Alternatively, Eq. (4.42) may be re-cast as

$$\tau_{comp} = \rho_B R / 3b\beta' C_{A,g} \quad (4.44)$$

where β' is the individual mass transfer coefficient during the pore diffusion step, defined as

$$\beta' = D/\Delta r \approx D/(R/2) \quad (4.45)$$

In this form, Eq. (4.44) defining the time taken for the solid particle to undergo complete conversion when a heterogeneous process goes on in the pore diffusion region is analogous to Eq. (4.32) derived for the surface diffusion region.

A heterogeneous process taking place in the pore diffusion region may largely be stepped up by increasing β' . This coefficient increases with increasing D and decreasing thickness, Δr , of the solid product layer. The coefficient of diffusion D is only slightly dependent on temperature; rather, it is decided by the porosity of the material and the tortuosity of the

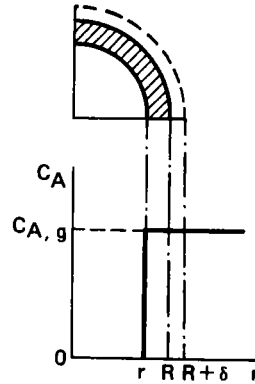


Fig. 4.6 Concentration profile of a gaseous reactant, with the rate of the heterogeneous process controlled by the chemical reaction

pores. It is far easier to control Δr . It is seen from Eq. (4.45) that the thickness of the solid product layer may be taken equal to half the original radius of the solid particle. As the particle decreases in size, Δr is reduced, but β' increases. In consequence, the resistance presented by pore diffusion can be brought down by comminuting the solid.

The rate-controlling step is the chemical reaction. If the surface and pore diffusion steps do not practically present any opposition to the process, no additional constraints are imposed on the chemical reaction involved, and the overall rate of the heterogeneous process solely depends on purely kinetic factors. Noting that for a process limited by a chemical reaction, $C_{A,c} = C_{A,s} = C_{A,g}$ (Fig. 4.6), we may write

$$w_A = -(1/S)(dn_A/d\tau) = k_s C_{A,c}^n = k_s C_{A,g}^n \quad (4.46)$$

Notably, for a 1st-order surface chemical reaction,

$$w_A = -(1/4 \pi r^2)(dn_A/d\tau) = k_s C_{A,g} \quad (4.47)$$

On replacing, as in the previous cases, the rate of reactant consumption $dn_A/d\tau$ in Eq. (4.47) with the rate of movement of the core boundary $dr/d\tau$, we get

$$-(1/4\pi r^2)(1/b)\rho_B 4\pi r^2(dr/d\tau) = k_s C_{A,g} \quad (4.48)$$

Hence,

$$\begin{aligned} \tau &= -(\rho_B/bk_s C_{A,g}) \int_R^r dr = (\rho_B/bk_s C_{A,g})(R - r) \\ &= (\rho_B R/bk_s C_{A,g})(1 - r/R) \end{aligned} \quad (4.49)$$

On recalling Eq. (4.30), we may re-write Eq. (4.49) as

$$\tau = (\rho_B R/bk_s C_{A,g})[1 - (1 - x_B)^{1/3}] \quad (4.50)$$

At $x_B = 1$, Eq. (4.50) yields the time τ_{comp} required for the solid particle of radius R to undergo complete conversion when a heterogeneous process takes place in the kinetic region

$$\tau_{comp} = \rho_B R / b k_s C_{A,g} \quad (4.51)$$

To sum up, for a heterogeneous process taking place in the kinetic region

$$\tau = \tau_{comp} [1 - (1 - x_B)^{1/3}] \quad (4.52)$$

The time to complete conversion, τ_{comp} , is a factor which decides to a large extent both the absolute and specific throughput of the reactor in which a heterogeneous process is effected. In the case on hand, it is a function of both R and $C_{A,g}$ which also appear in Eqs. (4.32) and (4.44) defining the time to complete conversion of solid particles when the process takes place in the surface and pore diffusion regions, and a function of the surface reaction rate constant k_s . An increase in k_s would bring about a sudden increase in the specific throughput of the reactor when the reaction takes place in the kinetic region. Since k_s mainly depends on temperature, the most convenient way to control a heterogeneous process limited by a chemical reaction is to vary the process temperature.

4.2.5 Identification of the Rate-Controlling Step

The computations involved in the design of a reactor for heterogeneous gas-solid processes (see Sec. 9.4) can conveniently be carried out if the rate-controlling step of the process is known. Then the residence time of the particle in the reactor will be connected to the fractional conversion of the solid reactant by a straightforward relation taking the form of Eq. (4.33), (4.43), or (4.52). As straightforward are the ways and means of controlling such a process. This is why it is important to identify the rate-controlling step of the process.

If the individual mass transfer coefficients β and β' and the rate constant k_s are known, we can compare their numerical values and say if there is a rate-controlling step in the process taking place under specified conditions, and if there is one, we may also say which step it is. As already noted, the rate-controlling step presents a maximum resistance. For example, if the rate-controlling action comes from surface diffusion, then

$$1/\beta \gg 1/\beta' \quad \text{and} \quad 1/\beta \gg 1/k_s \quad (4.53)$$

or

$$\beta \ll \beta' \quad \text{and} \quad \beta \ll k_s \quad (4.54)$$

If, on the other hand, the above quantities are of the same order of magnitude, there is no rate-controlling step, and the heterogeneous process is then said to take place in the *transition region*.

Most often, however, the exact values of β , β' and k_s are not known, and the design equations that could be used to find them are either lacking or hold for a very narrow range of variations in the process variables. In the circumstances, it is most convenient to identify the rate-controlling step by experiment. The techniques used for the purpose may arbitrarily be classed into two groups.

Methods based on the observation of how variations in the variables of a heterogeneous process affect its rate. Experimentally the rate-controlling step can be identified by observing changes in the rate of a heterogeneous process as a function of temperature T , the linear velocity u of the gas stream, and the degree of comminution $1/R$.

If, within a certain range of variations in its variables (T , u , and $1/R$), a heterogeneous process is limited by a chemical reaction, its rate will mainly be determined by the rate constant of the surface reaction, k_s , which increases exponentially with increasing temperature. In contrast, the individual mass transfer coefficients, β and β' , depend on temperature only slightly (in proportion to $T^{1/2}$). In consequence, if the linear velocity of the stream u and the particle size R remain constant with increasing temperature while the rate of the process rises abruptly, the process goes on in the kinetic region.

The kinetic region is typical of processes which occur at relatively low temperatures. If we consider the temperature dependence of the rate of a heterogeneous process over a wide temperature range (several hundred degrees) (Fig. 4.7), three characteristic regions may be singled out. These regions are:

(1) The temperature dependence is strong and nearly exponential. Obviously, in this temperature range the process is limited by the chemical reaction (the kinetic region).

(2) The temperature dependence is weak. The process is limited by surface or pore diffusion (the diffusion region).

(3) All the steps present about the same resistance (this is the transition region between the kinetic and diffusion regions).

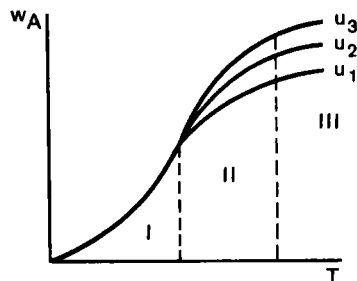


Fig. 4.7 Rate of a heterogeneous process as a function of temperature at constant linear velocity u of the gas and solid particle size R : I, kinetic region; II, transition region; III, diffusion region

$$u_3 > u_2 > u_1$$

If analysis of the temperature effect on the rate of a heterogeneous process shows that the temperature range of interest agrees with the diffusion region, it is important to decide which form of diffusion (surface or pore) is the rate-controlling one.

The rate of convective transfer strongly depends on fluid-dynamic factors. Therefore, an increase in the linear velocity of the gas stream relative to the solid particles, with R and T remaining constant, leads to a sudden increase in the rate of the process if it is limited by surface diffusion. The rate of a heterogeneous process as a function of temperature for several values of the linear velocity u is shown in Fig. 4.7.

The rate of pore diffusion should markedly rise when the solid phase is comminuted (because $\beta' = D/(R/2)$). If the temperature and the linear velocity of the stream have not been found to limit the rate of the process, but the comminution of the solid material does bring about an increase in the rate of the heterogeneous process, this is an indication that it goes on in the pore diffusion region — its rate is determined by diffusion into the pores of the solid.

Methods based on the comparison of experimental and theoretical time dependencies of $x_B(\tau)$. With these methods, the experimental kinetic dependence of the fractional conversion of the solid reactant on the residence time in the reactor, $x_B(\tau)$, is compared with its theoretical counterpart for the various regions in which the heterogeneous process may take place.

The theoretical dependences $x_B(\tau)$ take the following forms:

— for the surface diffusion region, in accord with Eq. (4.33)

$$x_B = \tau/\tau_{comp} \quad (4.55)$$

— for the kinetic region, in accord with Eq. (4.52)

$$x_B = 1 - (1 - \tau/\tau_{comp})^3 \quad (4.56)$$

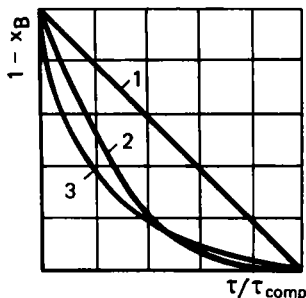


Fig. 4.8 Fractional conversion of a solid reactant as a function of solid-particle residence time, with the rate of the process controlled by: 1, external diffusion; 2, surface chemical reaction; 3, pore diffusion through "ash" layer

— for the pore diffusion region, in accord with Eq. (4.43)

$$1 - \tau/\tau_{comp} = 3(1 - x_B)^{2/3} - 2(1 - x_B) \quad (4.57)$$

which is a function specified in an implicit form.

Figure 4.8 shows three curves corresponding to Eqs. (4.55) through (4.57). Unfortunately, the difference in position between curves 2 and 3 which correspond to the pore diffusion and kinetic regions, respectively, is very small and comparable with experimental error.

Another method used to analyse the experimental dependences $x_B(\tau)$ and to compare them with their theoretical equations (4.33), (4.43) and (4.52) consists in that one uses the experimental values of x_B obtained at different times τ and computes the time required for the complete conversion of the solid particle, τ_{comp} , by the equations

$$\tau_{comp} = \tau/x_B(\tau) \quad (4.58)$$

(on the assumption that surface or external diffusion is the limiting step);

$$\tau_{comp} = \frac{\tau}{1 - 3[1 - x_B(\tau)]^{2/3} + 2[1 - x_B(\tau)]} \quad (4.59)$$

(on the assumption that pore diffusion is the limiting step), and

$$\tau_{comp} = \frac{\tau}{1 - [1 - x_B(\tau)]^{1/3}} \quad (4.60)$$

(on the assumption that the chemical reaction is the limiting step).

Under the specified operating conditions of a heterogeneous process, τ_{comp} has the physical meaning of a constant independent of the actual residence time of the solid particles in the reactor, τ . Therefore, if a limiting step does exist, analysis of experimental data on the basis of one of the above equations will show that τ_{comp} remains unchanged at any value of τ .

4.3 Heterogeneous Processes in a Gas-Liquid System (Gas-Liquid Reactions)

Gas-liquid reactions are heterogeneous processes involving chemical interaction between the reacting species one of which is in the gas (or vapour) phase, and the other in the liquid phase. The liquid may be a substance in solution, chemically interacting with the gaseous reactant. In some cases, the gas solute may react with the solvent.

Gas-liquid reactions are widely used in the chemical process industries. In some cases, they are used on their own as processes for the manufacture of desired products. Examples are the absorption of ammonia by a solution of nitric acid in the manufacture of ammonium nitrate or by a solution of sulphuric acid in the manufacture of ammonium sulphate (in fertilizer

manufacture); chlorination of liquid aromatic hydrocarbons (organic syntheses). In other cases, they are used as auxiliary steps in the purification of gas mixtures. Examples are the absorption of carbon dioxide, CO_2 , by aqueous solutions of monoethanolamine or potassium carbonate in order to scrub synthesis gas in the manufacture of ammonia; the absorption of sulphur dioxide, SO_2 , by solutions of ammonium sulphite and bisulphite in gas purification.

It is customary to treat gas-liquid reactions as absorption accompanied by a chemical interaction. With this approach, one may apply mass-transfer relationships to this group of chemical processes, assuming that the chemical reaction taking place at the interface between the gas and liquid phases or in the bulk liquid phase speeds up the absorption step. This in turn raises the overall mass transfer coefficient or the individual mass transfer coefficient from the gas to the liquid phase or from the liquid to the gas phase.

This opportunity of speeding up mass transfer is widely used in practice. The absorption step can substantially be accelerated by adding to the solvent such substances as will rapidly react with the constituents extracted from the gas phase. For example, CO_2 may be extracted from a gas mixture by absorbing it with water under pressure. When water is replaced with solutions of ethanolamines or carbonates which react with CO_2 , the rate of absorption can be increased manifold.

Description of the mass transfer between a gas and a liquid. In many cases when the concentration of the dissolved gas is low and the temperature and pressure are far from their critical values, the solubility of the gas in the liquid obeys Henry's law which states: The mass of gas dissolved by a given volume of solvent at a constant temperature is proportional to the pressure of gas with which the solvent is in equilibrium. Accordingly, the equilibrium partial pressure of the dissolved gas, $p_{A,e}$, above the solution is directly proportional to its concentration in the liquid phase, $C_{A,l}$:

$$p_{A,e} = H_A C_{A,l} \quad (4.61)$$

where the proportionality factor H_A is called the *Henry constant* or the coefficient of distribution of substance A between phases.

A plot showing variations in the partial pressure of reactant A in the gas phase and its concentration in the liquid phase is given in Fig. 4.9. The individual coefficient of mass transfer from the gas to the liquid is proportional to the driving force which is the difference in partial pressure of constituent A between the bulk gas phase, p_A , and the interface between the phases, $p_{A,b}$:

$$w_A = -(1/S)(dn_A/d\tau) = \beta_g(p_A - p_{A,b}) \quad (4.62)$$

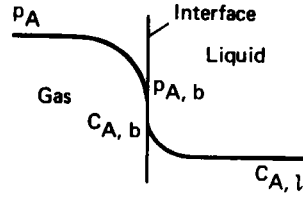


Fig. 4.9 Distribution of the partial pressure and concentration of gaseous solute A due to mass transfer between the phases

where β_g is the individual coefficient of mass transfer from the gas phase.

In turn, the individual coefficient of mass transfer from the liquid to the gas is

$$w_A = -(1/S)(dn_A/d\tau) = \beta_l(C_{A,b} - C_{A,l}) \quad (4.63)$$

where:

β_l = individual coefficient of mass transfer from the liquid phase

$C_{A,b}$ = concentration of solute A at the boundary between the phases

$C_{A,l}$ = concentration of solute A in the bulk liquid phase

In mass transfer computations it is usual to assume that a state of equilibrium exists at the interface. This amounts to assuming that the resistance to mass transfer across the interface may be neglected and that all of the opposition to mass transfer is concentrated in the gas layer adjacent to the interface, on the one hand, and in the bordering liquid layer, on the other.

In accord with Eq. (4.61), at equilibrium

$$C_{A,b} = p_{A,b}/H_A \quad (4.64)$$

In order to derive an equation for the rate of mass transfer which would take into account the resistance presented by both the liquid and gas phases, let us re-write Eqs. (4.62) and (4.63) as

$$w_A/\beta_g = p_A - p_{A,b} \quad (4.65)$$

$$w_A/\beta_l/H_A = p_{A,b} - H_A C_{A,l} \quad (4.66)$$

In Eq. (4.66), the concentration of the solute at the interface, $C_{A,b}$, is expressed in terms of the partial pressure of the same substance at the interface in accord with Eq. (4.64).

At equilibrium, the individual coefficients of mass transfer from the gas to the liquid phase or from the liquid phase to the gas are the same and equal to w_A , the overall mass transfer coefficient. *

Adding Eqs. (4.65) and (4.66) termwise, we obtain an equation which does not contain the unknown partial pressure at the boundary between the

* This assertion holds also for a heterogeneous process taking place under steady state conditions.

phases, $p_{A,b}$:

$$w_A (1/\beta_g + H_A/\beta_l) = p_A - H_A C_{A,l} \quad (4.67)$$

or

$$w_A = \frac{1}{1/\beta_g + H_A/\beta_l} (p_A - H_A C_{A,l}) \quad (4.68)$$

Equation (4.68) contains only quantities found by experiment: the partial pressure of the solute in the gas phase, p_A , the concentration of this species in the bulk liquid $C_{A,l}$ and the coefficient of mass transfer

$$K_m = 1/(1/\beta_g + H_A/\beta_l) \quad (4.69)$$

The individual mass transfer coefficients β_g and β_l in Eq. (4.69) can, as a rule, be found, using equations with dimensionless groups. * H_A is found from the equilibrium solubilities of gases.

When mass transfer takes place, the resistance may be distributed uniformly in the liquid or in the gas phase. It may also so happen that the resistance in the liquid phase or in the gas phase is predominant.

If the resistance is concentrated mainly in the gas phase, which means that $1/\beta_g \gg H_A/\beta_l$, Eq. (4.68) takes a simpler form:

$$w_A = \beta_g (p_A - H_A C_{A,l}) \quad (4.70)$$

If, on the other hand, the constituent A , on dissolving, rapidly reacts with the constituents present in the liquid phase, its concentration in the bulk liquid will be negligible and

$$w_A = \beta_g p_A$$

Whether or not the rate of a process is controlled by the mass transfer in one of the phases largely depends on the numerical value of H_A . At low values of H_A , that is, when the gas is highly soluble in the liquid, Eq. (4.61),

$$K_m \approx \beta_g \quad (4.72)$$

That is, as in the previous case, absorption is limited by the individual mass transfer coefficient in the gas phase.

At high values of H_A ,

$$K_m \approx \beta_l / H_A \quad (4.73)$$

That is, the resistance to mass transfer is concentrated in the liquid phase.

Kinetic models of gas-liquid reactions. Commercially, gases and liquids are reacted in continuous-flow reactors in which absorption is markedly af-

* When coefficients of mass transfer are found on model units, it is usual to determine the so-called volumetric coefficients of mass transfer, $\beta_l a$ or $\beta_g a$, where a [$\text{m}^2 \text{m}^{-3}$] is the specific interfacial surface area.

fectured by how well the reactants are being stirred. The vigorous agitation of a gas-liquid system leads to an increase in and the renewal of the interfacial surface area, thereby increasing the throughput of the reactor.

Agitation can be done in any one of several ways. One is by bubbling a gas through the liquid (as is done in tray-type towers) when the bubbles act as an agitating agent. A liquid can be agitated by mechanical stirrers used alone or in conjunction with bubbling (or sparging). The agitation of a liquid can be enhanced by letting it flow down a vertical or an inclined wall because it will then be flowing in a turbulent fashion. A liquid may also be sprayed into a gas stream to form droplets or squirted in jets.

In all of such cases, a rigorous description of absorption calls for a simultaneous solution of equations for diffusion and convective transfer, kinetic equations, etc. However, it is often very difficult not only to solve, but even to set up such a system of equations. In practice, therefore, resort is made to simplified models which, however, agree well with experimental data. The most commonly used models are the film model and the surface renewal model.

The *film model* is based on the assumption that at the liquid surface bordering on the gas there is a stationary film (a diffusion layer) of thickness δ . Within this film, the gaseous reactant is transported solely by molecular diffusion while convective transfer is nonexistent. * It is further assumed that the bulk liquid beyond the film has a uniform composition due to perfect mixing while the concentration of the solute changes from $C_{A,g}$ (the constant concentration in the gas phase) to $C_{A,l}$ (its concentration in the bulk liquid) inside the film (Fig. 4.10).

When no chemical reaction takes place between the solute A and the solvent, constituent A will have a linear concentration profile (line I in Fig. 4.10). The mass transfer from a gas to a liquid across the boundary film is described by Fick's law for molecular diffusion (Fick's first law):

$$w_A = -(1/S)(dn_A/d\tau) = D \, dC_A/dr \quad (4.74)$$

Under steady state conditions, the flux across the plane will be constant, and so the coefficient of molecular diffusion will likewise be constant:

$$dC_A/dr = \text{const} = (C_{A,g} - C_{A,l})/\delta \quad (4.75)$$

Then,

$$w_A = (D/\delta)(C_{A,g} - C_{A,l}) = \beta_l(C_{A,g} - C_{A,l}) \quad (4.76)$$

where β_l is the individual mass transfer coefficient in the diffusion film, defined as

$$\beta_l = D/\delta \quad (4.77)$$

* This assumption agrees with the "reduced" surface film model used in the discussion of the surface diffusion step in gas-liquid reactions (see Sec. 4.2).

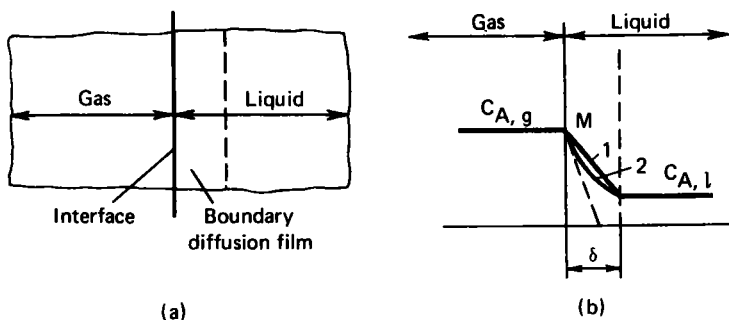
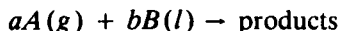


Fig. 4.10 Sketch of (a) the film model and (b) concentration profile of solute A : 1, without a reaction; 2, with a reaction

When the solute A reacts with the reactant B in the liquid phase,



(where 'l' stands for 'liquid'), the concentration of reactant A in the boundary film decreases not only due to diffusion, but also because it is used up in the reaction. The concentration profile in the boundary layer is therefore curved (curve 2 in Fig. 4.10b). This leads to an increased concentration gradient of the reactant at the interface — the numerical value of the slope of the tangent to the $C_A(z)$ curve at point M , equal to $\text{grad } C_A$, increases. As a result, the individual coefficient of mass transfer from the gas to the liquid phase is increased

$$w_A = D \text{ grad } C_A$$

which, as already noted, is a distinction of gas-liquid reactions.

Within the framework of the film model, we may, at least formally, introduce a factor which accounts for the acceleration of absorption owing to the chemical reaction. The curved concentration profile of reactant A inside the boundary film in the case of a reaction may arbitrarily be approximated by a broken line (Fig. 4.11). Under this approximation, the concentration of the reactant changes inside a film of thickness δ' . A 'decrease' in

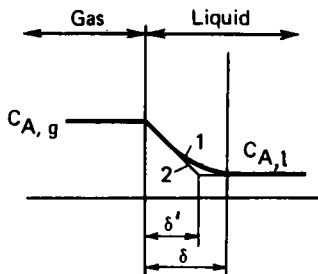


Fig. 4.11 Approximation of a nonlinear concentration profile for a process with a chemical reaction: 1, real (nonlinear); 2, approximation

the film thickness leads to an increase in the individual mass transfer coefficient:

$$\beta_l' = D/\delta' = \varepsilon(D/\delta) = \varepsilon\beta_l \quad (4.78)$$

where:

β_l' = individual mass transfer coefficient in the case of a chemical reaction

ε = absorption acceleration factor in the case of a chemical reaction

Recalling Eq. (4.78), we may re-write Eq. (4.69) for K_m as

$$K_m = \frac{1}{1/\beta_g + H_A/\varepsilon\beta_l} \quad (4.79)$$

The film model has been refined to yield a *double-film model*. In accord with this model, it is assumed that the boundary diffusion layer adjacent to the interface exists on both sides, that is, on the liquid-phase side and the gas-phase side.

The film model describes gas-liquid reactions only approximately. Actually, the concentration of the solute changes not only inside the very thin boundary film varying, as it does, in thickness from one point to another, but also in the bulk stream. As experience has shown, however, quantitative computations based on the film model differ only slightly from the results obtained when far more sophisticated models are used. Therefore, it is often warranted to use the film model, the more so that it involves a relatively simple body of mathematics.

The surface-renewal (or penetration) models are based on the assumption that at some intervals of time the liquid elements at the interface are replaced with liquid from the deeper layers where the composition is the same as the average composition of the bulk liquid. As long as a liquid element stays at the surface and in contact with the gas, the gas is absorbed by the liquid in the same way as if this element were stationary and had infinite depth. In this model, the rate of absorption is a function of the presumed "residence time" of the liquid element at the interface. Initially, when $\tau = 0$, the rate is high, but it decreases as the residence time increases.

Thus, within the framework of the penetration model, the absorption of a gas by a liquid is regarded as an unsteady process.

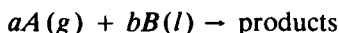
In an early form of the penetration model it was assumed that every element of liquid at the surface remains in contact with the gas before it is replaced by another liquid element from the bulk during one and the same time span, τ . In the meantime, every unit area of the liquid element absorbs one and the same quantity Q of gas, which agrees with the assumption that the liquid is stationary. The average rate of absorption is then Q/τ .

Actually, the residence time of the individual liquid elements at the interface does not remain constant. Different penetration models assume dif-

ferent distributions for the residence time of the individual elements of liquid.

The penetration models for the absorption of gases by stirred liquids appear to be more realistic. However, they use far more sophisticated body of mathematics than the film model does. Moreover, the quantitative predictions made on the basis of the film model differ only slightly from the computations based on the penetration models.

Determining the absorption acceleration factor in the case of a chemical reaction. Let us see how the reaction



affects the absorption of gaseous reactant A by the liquid containing reactant B . Our computations will be based on the film model. As an example, we will take a 1st-order reaction whose kinetics is described by the equation

$$w_{rA} = kC_A \quad (4.80)$$

Many gas-liquid reactions may be regarded as pseudo-1st-order reactions. Suppose that the true rate equation has the form

$$w_{rA} = kC_A C_B^n \quad (4.81)$$

As a rule, the concentration of species B in the liquid phase is substantially greater than that of species A in the bulk liquid contained in a well-stirred reactor, including the diffusion layer where the chemical reaction takes place. Then, Eq. (4.81) may be re-cast as

$$w_{rA} = k' C_A \quad (4.82)$$

where

$$k' = kC_B^n \quad (4.83)$$

is the rate constant of the pseudo-1st-order reaction and includes the practically constant concentration of reactant B in addition to the true rate constant of reaction.

Now let us see what happens in an elementary volume inside the laminar film where a gas-liquid reaction takes place. We select this volume as a parallelepiped whose thickness is $\delta = dz$ whose base has a surface area S , and which is perpendicular to the direction of diffusion (Fig. 4.12). Owing to molecular diffusion from the gas phase, the following quantity of reactant A enters the element of volume per unit time:

$$-DS(\partial C_A / \partial z) \quad (4.84)$$

which is found by Fick's law. On the opposite side, the following quantity of species A leaves the parallelepiped per unit time

$$-DS[\partial C_A / \partial z + (\partial^2 C_A / \partial z^2) dz] \quad (4.85)$$

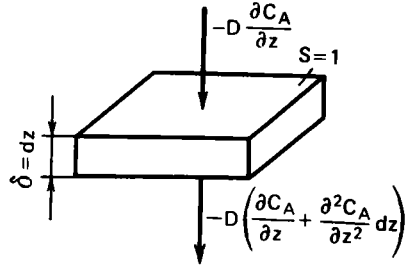


Fig. 4.12 To writing a material balance over an elementary volume inside the diffusion film

Some quantity of species A is used up in the chemical reaction effected in the elementary volume. The quantity of reactant used up in a reaction is proportional to the reaction rate and reaction volume:

$$w_{rA} S dz = (k C_A) S dz \quad (4.86)$$

Under steady state conditions, the quantity of substance A entering the elementary volume due to molecular diffusion is equal to that used up in the chemical reaction and carried away with the diffusion stream:

$$-DS(\partial C_A / \partial z) - \{-DS[(\partial C_A / \partial z) + (\partial^2 C_A / \partial z^2) dz] + w_{rA} S dz\} = 0 \quad (4.87)$$

Hence,

$$D(d^2 C_A / dz^2) - k C_A = 0 \quad (4.88)$$

or

$$d^2 C_A / dz^2 - (k/D) C_A = 0 \quad (4.89)$$

Equation (4.89) is a linear second-order differential equation. We will solve it subject to the following boundary conditions:

(1) $C_A = C_{A,b}$ at $z = 0$ (at the interfacial surface)

(2) $C_A = C_{A,l}$ at $z = \delta$ (at the boundary separating the diffusion film and the bulk liquid), such that, in accord with Eq. (4.77),

$$\delta = D / \beta_l \quad (4.90)$$

where β_l is the individual mass transfer coefficient in the liquid film for physical absorption.

We seek the particular solution of Eq. (4.89) in the form

$$C_A = \exp(az)$$

Then, on substituting this solution in Eq. (4.89), we get the characteristic equation

$$a^2 - k/D = 0$$

Hence,

$$a = \pm (k/D)^{1/2}$$

That is, the particular solutions of the differential equation (4.89) are the functions

$$C_A = \exp [z(k/D)^{1/2}]$$

and

$$C_A = \exp [-z(k/D)^{1/2}]$$

The general solution of Eq. (4.89) may be written as a linear combination of the two particular solutions

$$C_A = M_1 \exp [z(k/D)^{1/2}] + M_2 \exp [-z(k/D)^{1/2}] \quad (4.91)$$

The constants of integration can be found from the boundary conditions. At $z = 0$,

$$C_A = C_{A,b} = M_1 + M_2$$

Hence,

$$M_2 = C_{A,b} - M_1 \quad (4.92)$$

At $z = \delta$,

$$C_A = C_{A,l} = M_1 \exp [\delta(k/D)^{1/2}] + M_2 \exp [-\delta(k/D)^{1/2}]$$

In view of Eqs. (4.90) through (4.92),

$$C_{A,l} = M_1 \exp [(D/\beta_l)(k/D)^{1/2}] + (C_{A,b} - M_1) \exp [-(D/\beta_l)(k/D)^{1/2}] \quad (4.93)$$

On designating

$$M = Dk/\beta_l^2 \quad (4.94)$$

we obtain from Eq. (4.93)

$$\begin{aligned} M_1 &= \frac{C_{A,l} - C_{A,b} \exp [-M^{1/2}]}{\exp (M^{1/2}) - \exp (-M^{1/2})} \\ &= \frac{C_{A,l} - C_{A,b} \exp (-M^{1/2})}{2 \sinh (M^{1/2})} \end{aligned} \quad (4.95)$$

where

$$\sinh (M^{1/2}) = [\exp (M^{1/2}) - \exp (-M^{1/2})]/2$$

The other constant of integration can be obtained from Eq. (4.95)

$$M_2 = \frac{C_{A,b} \exp (M^{1/2}) - C_{A,l}}{2 \sinh (M^{1/2})} \quad (4.96)$$

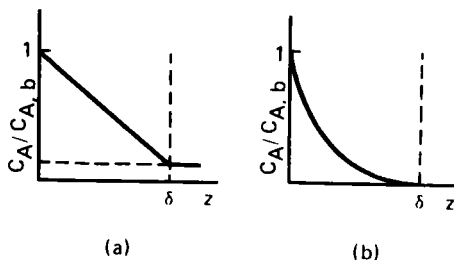
Then the solution of the differential equation (4.89) takes the form

$$C_A = \frac{C_{A,l} \sinh [z(k/D)^{1/2}] + C_{A,b} \sinh [M^{1/2} - z(k/D)^{1/2}]}{\sinh (M^{1/2})} \quad (4.97)$$

The typical concentration-versus-distance profiles obtained on the basis of Eq. (4.97) are shown in Fig. 4.13.

Fig. 4.13 Concentration profiles of a gaseous solute for a 1st-order reaction in the liquid phase, as found by Eq. (4.97):

a, some of the unreacted gas diffuses into the bulk liquid, $M^{1/2} = 1$; *b*, the chemical reaction is nearly completed in the diffusion film, $M^{1/2} = 5$



When determining the reaction acceleration factor due to a chemical reaction, the rate of physical absorption should be compared with the rate of chemisorption. The rate of absorption per unit of interfacial surface area in the presence of a chemical reaction and subject to Eq. (4.97) can be found as follows:

$$w_A = -D(dC_A/dz)_{z=0} = -D \frac{C_{A,i} - C_{A,b}(k/D)^{1/2} \cosh(M^{1/2})}{\sinh(M^{1/2})} \quad (4.98)$$

where:

$$\cosh(M^{1/2}) = [\exp(M^{1/2}) + \exp(-M^{1/2})]/2$$

Since in accordance with Eq. (4.94)

$$D(k/D)^{1/2} = (kD)^{1/2} = \beta_l M^{1/2}$$

we may write

$$w_A = \beta_l [C_{A,b} - C_{A,i}/\cosh(M^{1/2})][M^{1/2}/\tanh(M^{1/2})] \quad (4.99)$$

Equation (4.99) describing absorption accompanied by a chemical reaction differs from Eq. (4.63) describing physical absorption:

$$w_A = \beta_l (C_{A,b} - C_{A,i})$$

When a fast chemical reaction takes place in the film and $C_{A,i} = 0$, Eq. (4.99) takes a simpler form:

$$w_A = \beta_l C_{A,b} [M^{1/2}/\tanh(M^{1/2})] \quad (4.100)$$

and the absorption acceleration factor ε may be found by equating Eqs. (4.100) and (4.63) at $C_{A,i} = 0$

$$\varepsilon = \frac{\beta_l C_{A,b} M^{1/2}/\tanh(M^{1/2})}{\beta_l C_{A,b}} = M^{1/2}/\tanh(M^{1/2}) \quad (4.101)$$

or, at $M^{1/2} \gg 1$ * [because then $\tanh(M^{1/2})$ tends to unity],

$$\varepsilon \approx M^{1/2} = (kD)^{1/2}/\beta_l \quad (4.102)_s$$

* In the case of a fast chemical reaction,

$$M^{1/2} = (kD)^{1/2}/\beta_l \gg 1$$

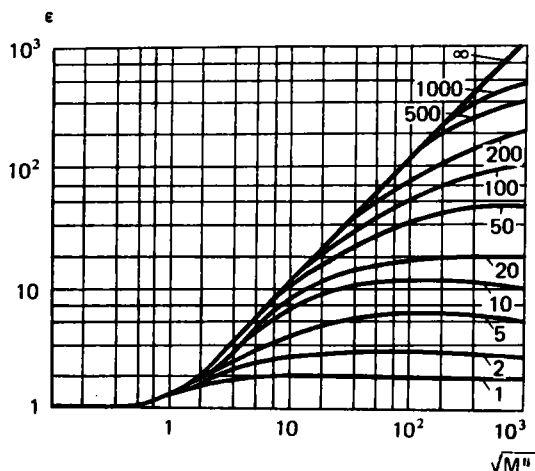


Fig. 4.14 Diagram of absorption acceleration factor ϵ for fast 2nd-order reactions (the numbers on the curves are the values of the group $aC_{B,l}D_B/bC_{A,b}D_A$)

Thus, it is seen that an increase in the reaction rate constant k leads to a greater absorption acceleration factor ϵ .

A similar result can be obtained on the basis of the penetration model.

The absorption acceleration factor may likewise be computed for higher-order reactions. As an example, Fig. 4.14 shows a plot of ϵ for a 2nd-order chemical reaction. In this case, ϵ is a function of the dimensionless groups

$$(M'')^{1/2} = (kDC_B/\beta_l^2)^{1/2}$$

and

$$aC_{B,l}D_B/bC_{A,b}D_A$$

where a and b are the stoichiometric coefficients, D_A and D_B are the molecular diffusion coefficients of reactants A and B , respectively.

Chapter Five

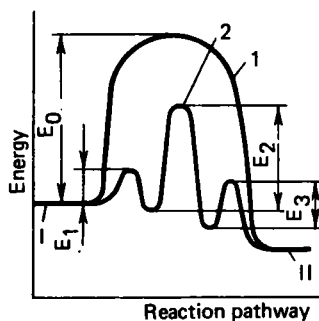
HETEROGENEOUS CATALYTIC PROCESSES

In the overwhelming majority of state-of-the-art chemical technologies, the reaction rate is controlled through the use of catalysts.

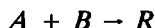
A catalyst is a substance that, on repeatedly entering into intermediate reactions with the reactants and products, changes the reaction mechanism and increases the speed with which equilibrium is attained.

Fig. 5.1 Energy diagrams of a catalyzed and an uncatalyzed reaction:

Energy levels: *I*, for reactants; *II*, for products; *1*, reaction pathway without a catalyst; *2*, reaction pathway with a catalyst



The manner in which a catalyst affects the mechanism of a chemical reaction can be illustrated, using a hypothetical example. We consider the single-step reaction



for which the activation energy is E_0 . In the energy diagram of Fig. 5.1 the course of the reaction is represented by curve *1*. In the presence of a catalyst, the mechanism of the reaction is changed: it is now effected via several intermediate steps (curve *2*). For example, the first step may be the formation of an intermediate activated complex



where '*Kt*' stands for 'catalyst'. Then the activated complex reacts with the other reactant to form a complex made up of the catalyst and the product:



The last step is the decomposition of the complex *RKt* with the formation of the product *R* and the release of the catalyst which then can participate in another cycle:



For each of the above consecutive (or series) steps there is an activation energy of its own: E_1 , E_2 , and E_3 (curve *2* in Fig. 5.1). As a rule, however, the height of each of these potential barriers is lower than E_0 . Thus, in the presence of a catalyst, the reaction proceeds along a pathway which is energetically more favourable, and so the process is carried out at a higher rate.

The initial energy state (*I*) and the final energy state (*II*) of the reaction mixture with and without a catalyst remain the same. In consequence, the following may be stated.

A catalyst cannot change the state of chemical equilibrium because it does not depend on the pathway of the reaction.

A catalyst only acts to increase the rate at which a state of equilibrium is attained. A catalyst is able to speed up only those processes which are thermodynamically feasible, but it cannot initiate thermodynamically unfeasible reactions.

Some chemical reactions cannot practically take place unless a catalyst is added to the reaction mixture, because, say, the activation energy is too high. It would seem that the high energy barrier could be overcome by raising the kinetic energy of the molecules, that is, by raising the temperature of the reaction mixture. Unfortunately, a rise in temperature leads to a backward shift in the position of equilibrium for many reversible exothermic reactions, thereby rendering them unallowable thermodynamically. In such cases, the use of a catalyst is in fact a necessity. A catalyst brings down the activation energy of the reaction so that it can be carried out at substantially lower temperatures.

An example is the synthesis of ammonia where the activation energy is very high, being around 280 kJ mol^{-1} . * To overcome such a high energy barrier, the reactants would have to be heated to a temperature of over 1000°C , but at such temperatures the equilibrium conversion is negligible even at high pressures.

In the presence of an iron-based catalyst the activation energy in ammonia synthesis is brought down to about 160 kJ mol^{-1} so that the process can be carried out at a sufficiently high rate at temperatures as low as $400\text{--}500^\circ\text{C}$ and at high pressures, with the conversion of the reactants being as high as 20–35%.

Catalysts play a very important part in complex reactions. The point is that they possess the valuable property of specificity (or selectivity) owing to which a catalyst will favour one particular mechanism or pathway of the reaction over others. An example is the cracking of petroleum which involves a system of complex consecutive (or series) and concurrent (or parallel) reactions. The process would be hardly feasible without selective zeolite catalysts which steer the process towards the production of high-grade petrol.

Catalytic reactions are classed into two large groups: homogeneous and heterogeneous. Heterogeneous catalytic reactions are used most in the chemical process industries. Among them, the overwhelming majority of reactions take place at the interface which is the surface of a solid catalyst immersed in a gaseous or liquid reaction mixture. A major advantage of

* It is to be noted that the activation energy E_0 for ammonia synthesis cannot be obtained by direct experiment, but this can be done for the reverse reaction — that of ammonia decomposition. Then, knowing that the difference in activation energy between the forward and reverse reactions is ΔH , one can readily find E_0 .

these processes is simplicity in separating the reaction products and the catalyst for re-use.

In the discussion that follows, emphasis will be placed on the kinetics of heterogeneous catalytic reactions with special reference to solid-catalyzed gas-gas reactions.

5.1 Operating Characteristics of Solid Catalysts

It is a formidable task to pick the right catalyst for a commercial chemical process. For one thing, catalysts are highly specific with respect to particular chemical reactions. Existing theories of catalysis trace this specificity to a number of factors involving energy and geometry — because of them a catalyst can affect the rate of only one reaction or a very narrow group of reactions. But although the theory of catalytic processes has made an impressive headway in the recent decades, a rigorously scientific choice of a catalyst for a particular chemical process is not always possible.

Solid catalysts are usually highly porous substances with an extended internal surface, a high porosity, and a specific crystalline structure. All this contributes to their activity, specificity, and some other operating characteristics.

Let us take a closer look at some characteristics of solid catalysts.

Activity. If several catalysts are available, the choice will usually be the one most active, provided it satisfies the other basic operating requirements.

The activity of a catalyst is a measure of the accelerating effect that it has on the rate of a given reaction.

Because catalytic processes are many and diverse, a single quantitative criterion of activity is non-existent. One way to measure the activity of a catalyst is to find the ratio between the rate constants of a catalyzed and an uncatalyzed reaction:

$$A = k^{Kt} / k = \frac{k_0^{Kt} \exp (-E^{Kt} / RT)}{k_0 \exp (-E_0 / RT)} \quad (5.1)$$

where:

A = activity

k^{Kt} = rate constant of the catalyzed reaction

k = rate constant of the uncatalyzed reaction

k_0^{Kt} = pre-exponential (frequency) factor of the catalyzed reaction

k_0 = pre-exponential (frequency) factor of the uncatalyzed reaction

E^{Kt} = activation energy of the catalyzed reaction

E_0 = activation energy of the uncatalyzed reaction

It follows from Eq. (5.1) that the activity of a catalyst increases with the decrease in the activation energy caused by the presence of the catalyst. It should be remembered, however, that a catalyst will usually change not only the activation energy, but also the pre-exponential (frequency) factor. The increase in activity due to a reduction in the activation energy is held back by the decrease in $k_0^{K'}$ in comparison with k_0 (a compensation effect is said to take place).

The measurement of activity by Eq. (5.1) is applicable only if k and $k^{K'}$ are expressed in the same units, that is, if the catalyzed and uncatalyzed reactions are of the same order. In the case of reactions which cannot take place without a catalyst because of a very high activation energy, Eq. (5.1) cannot be used to find the activity because $k = 0$ and $A = \infty$ for any catalyst. With such reactions, the activity of a catalyst may quantitatively be evaluated in terms of the rate of reaction or the rate constant of the catalyzed reaction, as measured under comparable conditions. For example, given certain process conditions, the activity of a catalyst may be stated in terms of the quantity of the substance reacted per unit time per unit surface of the catalyst (the catalyst's capacity), the conversion of the reactants under standard conditions, etc.

✓ **Kindling point.** This is the second most important characteristic of a catalyst after its activity.

(The kindling point is the minimum temperature at which a catalytic process goes on at a rate sufficient for commercial purposes.)

From a chemical-engineering point of view, preference should be given to catalysts having a low kindling point because less energy will have to be then expended to preheat the reaction mixture.

For exothermic reactions, the concept of kindling point can be defined quantitatively. The lower the temperature of a process, the lower the rate of reaction, and so less heat is given up. At some minimal temperature (the kindling point), the rate at which heat is generated becomes equal to the rate at which this heat is withdrawn (that is, to the quantity of heat expended to preheat the reaction mixture and the heat carried off with the reaction products). Thus, the kindling point for an exothermic reaction is the minimal temperature at which the process will proceed on its own, that is, with no heat input from without.

A low kindling point is especially valuable in the case of reversible exothermic reactions — the position of equilibrium can then be shifted towards the reaction products.

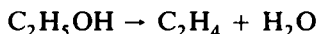
Specificity. Complex catalytic reactions may follow several thermodynamically feasible routes with the formation of a great number of products. Which route is actually followed depends on the catalyst used —

it is not necessarily the most favourable thermodynamically among the several likely routes.

The specificity (or selectivity) of a catalyst refers to its property to speed up the main reaction in the presence of several side reactions.

Quantitatively, the specificity of a catalyst may be evaluated as the selectivity of a process (see Sec. 1.2), which may be integral or differential.

When several parallel (concurrent) reactions take place at the same time, one may pick a catalyst best suited for each of them. For example, when passed over alumina (aluminium oxide) or thoria (thorium oxide), ethanol decomposes predominantly into ethylene and water according to the scheme



When passed over silver, copper or some other metal, ethanol undergoes practically only dehydrogenation with the formation of acetaldehyde:



When a mixed catalyst is used ($\text{Al}_2\text{O}_3 + \text{ZnO}$), it has a sufficiently high specificity for dehydration and dehydrogenation to take place, with the formation of butadiene according to the scheme



Specificity depends not only on the catalyst used, but also on the operating conditions, the region within which the heterogeneous catalytic process goes on (this may be the kinetic region, the surface-diffusion region, or the pore-diffusion region), etc.

The porous and crystalline structure of the catalyst. The porous structure is an important asset of a catalyst. It can be described in terms of the size and shape of pores, porosity (the ratio of the volume of voids to the total volume of a catalyst sample), the specific surface of a catalyst (the ratio of the exposed area of a catalyst sample to its mass or volume).

An important consideration in the selection of a solid catalyst for heterogeneous gas-gas reactions is the accessibility of the catalyst's surface to the reacting gases. The greater the exposed area, the greater the rate at which the reactants will be used up with the same quantity of catalyst.

A commercial catalyst should always have an extended internal surface. Otherwise, its external surface, which is small, would be poisoned quickly, and the catalyst would lose its activity. The internal surface area increases in proportion to the porosity of a catalyst and in inverse proportion to the pore size. Existing catalysts have a large specific surface (up to $10\text{--}100 \text{ m}^2 \text{ g}^{-1}$).

In some cases it may so happen, however, that the size distribution of pores is such that some of the catalyst's surface is inaccessible to large

reacting molecules. Additionally, the rate at which the reactants are converted to products may be reduced due to a slow-down in the diffusion of the reactants inside the pores.

For catalysts to have an extended porous structure, they are given a special treatment during manufacture. The starting materials are preferably natural or man-made highly porous adsorbents (such as aluminosilicates, zeolites, silica gel, activated carbon, etc.). Sometimes these materials are used as a support, with their surface coated by active components.

No less important than a porous structure is the crystalline structure of catalysts. Crystalline modifications of the same substance may strongly differ in catalytic activity. For example, the conversion of gamma- Al_2O_3 to alpha- Al_2O_3 will reduce the activity of the substance by several orders of magnitude as a dehydrogenation catalyst.

Catalyst promoters and poisons. The addition of a very small quantity (a fraction of one per cent) of some substances to a catalyst may often enhance or degrade its activity by several orders of magnitude. In the former case, the catalyst is said to be *promoted*, and in the latter, *poisoned*.

Solid catalysts may be promoted by more than one mechanism. The promoter may react with the catalyst to form on its surface several products which have a higher catalytic activity. Or it may alter the conditions in which the catalyst interacts with the reactants at points of contact between the main component and the promoter. Furthermore, a promoter may increase the degree of dispersion or stabilize the porous and crystalline structure of the catalyst, etc.

For example, the catalytic activity of V_2O_5 towards the oxidation of sulphur dioxide is enhanced by a factor of several hundreds when sulphates of alkali metals are added in small amounts. When 2 or 3% Al_2O_3 is added to the ammonia synthesis catalyst, a stable geometric structure is produced, which remains unaltered under the influence of the reaction mixture for a long time.

In contrast, catalytic poisons bring down the activity of catalysts to a point where a given catalytic process can no longer be of practical value. For example, if the feed gas used in the oxidation of SO_2 over the vanadium catalyst carries 4 or 5 mg m^{-3} of SiF_4 , the catalytic activity will be drastically reduced.

This agrees well with the theory of active centres. As it tells us, a catalyst displays its activity not over the entire surface of its grains, but at definite areas, called *active centres* (or *sites*), which match the reacting molecules in terms of energy and geometry. Catalytic poisons block these centres by reacting with them and forming surface chemical compounds.

Poisoning may be reversible (or temporary) and irreversible (or perma-

ment). With reversible poisoning, the activity of the catalyst is gradually restored if the reaction mixture does not contain a poison any more. With irreversible poisoning, a fresh portion of the reaction mixture fails to restore the activity. One and the same substance may cause reversible and irreversible poisoning, depending on how long it has been acting, how much of it is present in the reaction mixture, and the temperature at which the process goes on.

As an example, for the iron ammonia synthesis catalyst the poisons are oxygen and oxygen-carrying compounds (CO , CO_2 , and H_2O). If the feed gas passed over the catalyst at a pressure of 30 MPa and a temperature of 450 °C carries $1 \times 10^{-2}\%$ CO, the catalyst activity drops by 25% in six days. However, the catalyst activity can be restored in 24 hours by using a pure feed gas. When the feed gas contains $5 \times 10^{-2}\%$ CO, the catalyst activity falls by 67% in 3 days, but it is fully restored in 4 days by operation with a pure gas. At 500 °C and an oxygen content of $5 \times 10^{-3}\%$, the NH_3 concentration in the exit gas falls by 4%, and a pure gas fails to restore the original activity of the catalyst.

As a way of extending the useful life of catalysts under industrial conditions, provisions are made in the plant layout for a careful removal of catalytic poisons from the reacting species (for example, compounds of arsenic and fluorine in the manufacture of sulphuric acid; CO , CO_2 and sulphur compounds in the manufacture of ammonia, etc.).

Sometimes, a catalyst may be poisoned by the by-products of a reaction. For example, in reactions involving organic compounds (such as cracking, dehydrogenation, isomerization), a catalyst may often be poisoned by 'coke' (a high-carbon polymer deposit) that covers the surface of the catalyst grains. It can be removed by alternating a catalysis cycle with a regeneration cycle when the catalyst is blown with air at elevated temperature so as to convert the carbon to CO_2 .

5.2 Basic Steps and Kinetics of Heterogeneous Catalytic Processes

A heterogeneous catalytic reaction taking place at the surface of a solid catalyst is a complex, multi-step process. The observed overall rate of a catalytic reaction depends on the relative rates of the individual steps usually differing from one another both physically and chemically.

Let us consider the basic steps involved in the interaction between a gaseous reactant and a grain of a porous catalyst (Fig. 5.2).

Step 1. As is the case with a heterogeneous uncatalyzed process, the first to occur is the diffusion of the gaseous reactant from the bulk stream to the external surface of the catalyst grain through the gaseous film in

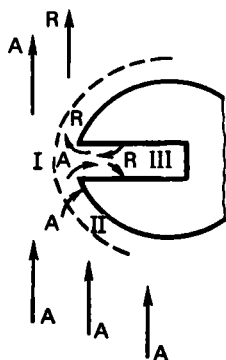


Fig. 5.2 Partial view of a catalyst grain:
I, gas stream passing over the catalyst grain; *II*, gaseous boundary film; *III*, pore inside the catalyst grain; *A*, reactant; *R*, product

which the concentration of the reactant is lower and that of the product is higher than they are in the bulk stream. This is the *external* (or *surface*) *diffusion step*.

Step 2. The greater proportion of gaseous-reactant molecules diffuse inside the pores of the catalyst. Quite aptly, this step may be called the *pore diffusion step*. The rate at which the molecules diffuse through the porous medium is a small fraction of their travel velocity. This is because the molecules collide with the pore walls and other molecules as they move through the catalyst, and this renders their motion totally random. According to the relative magnitude of the mean free path and the pore diameter and also the pressure drop across a pore, there may be three types of diffusion: free diffusion, Knudsen diffusion, and forced diffusion. All of them may be described by the equations of molecular diffusion (Fick's laws).

The next three steps are pivotal in the course of a catalytic process. Collectively, they may be regarded as a surface chemical reaction. These steps may take place simultaneously with the previous (diffusion) steps, and do so both at the external surface of the catalyst grains and, primarily, at the internal surface of the pores.

Step 3. The reacting molecules are adsorbed on the surface of the catalyst. Adsorption is a process associated with a decrease in the quantity of gas (the adsorbate) when it comes in contact with a solid (the adsorbent) and resulting in that the gas at the surface of the solid is made somewhat denser. There may be *physical adsorption* and *chemical adsorption*, or *chemisorption*, depending on the nature of the forces that bring about this concentration of the adsorbate molecules at the surface of the solid. If these forces are of the same nature as molecular interaction in gases, liquids and solids, physical adsorption is said to take place. If the forces responsible for the adsorption are of chemical nature, chemical adsorption is said to occur — as a result of it, the adsorbate molecules lose their identity on forming surface compounds with the adsorbent.

In catalytic processes, chemisorption, or *activated adsorption*, is predominant. It results in the formation of an activated adsorption complex — an unstable intermediate formed by the reactant and the catalyst. If the chemical bond between the reactant and the adsorbent is very strong, it will oppose the decomposition of the complex leading to the formation of products. If, on the other hand, the bond between the adsorbent and the adsorbate is weak and very close in its nature to physical adsorption, the bonds in the adsorbate molecule are not loosened and there is no reduction in the activation energy of the catalyzed process in comparison with its uncatalyzed counterpart.

Step 4. The adsorption step is directly followed by the *surface chemical reaction* proper. It consists in that either the activated adsorption complex is regrouped or one adsorbed reactant reacts with the molecules of the other reactant. The mechanism of this reaction may differ from one case to the next, and so will the applicable rate equation. The surface reaction ends up in the formation of an adsorbed product.

Step 5. The next step is the *desorption of the product* from the surface of the catalyst. The specific properties of the catalyst manifest themselves during this step as well: the energy required for a bond to be formed between the adsorbed product and the adsorbent must be such that the desorption in the bulk would not be hampered.

Step 6. The desorbed gaseous products diffuse from the pores to the outer surface of the catalyst grain (*reverse pore diffusion*).

Step 7. The gaseous products diffuse from the surface of the catalyst grain into the gas stream through the boundary film surrounding the grain (*reverse external diffusion*).

As we have seen, a heterogeneous catalytic process involves an intricate pattern of series and parallel reactions differing in nature from one another. As with uncatalyzed heterogeneous processes, one of the steps may slow down the overall process more than any others. If so, the other steps will 'adjust' their rates to the slowest step which may be called the rate-controlling (rate-determining or limiting) step.

The effect of mass transfer through the gas phase. The reactants prior to adsorption and the reaction products following desorption must be transported from the gas stream to the surface of the catalyst grain or the other way around. If the reaction takes place in a continuous-flow system, the velocity of the gas stream is usually sufficient for the mass transfer to proceed by eddy diffusion. In such a case, the overall rate of the process is independent of, or only slightly dependent on, the rate of external diffusion. When the gas flow is non-turbulent, the rate of mass transfer may be relatively low, and the catalytic reaction may be slowed down by external

diffusion which is an undesirable development when the process involved is carried out in an industrial reactor.

A catalytic process will take place in the external diffusion region when the catalyst grains are large in diameter, the linear velocity of the gas stream relative to the catalyst is low, and the temperature of the process is very high.

Then the reactant concentration, $C_{A,s}$, and the product concentration, $C_{R,s}$, at the external surface of the catalyst grain drastically differ from their counterparts in the bulk gas stream, $C_{A,g}$ and $C_{R,g}$:

$$C_{A,s} \ll C_{A,g} \quad (5.2)$$

$$C_{R,s} \gg C_{R,g} \quad (5.3)$$

The change of concentration, $\Delta C_A = C_{A,g} - C_{A,s}$ and $\Delta C_R = C_{R,s} - C_{R,g}$, takes place in the boundary diffusion layer whose thickness δ is a function of several factors. For example, for a laminar flow pattern,

$$\delta = a \text{Re}^{-0.5}$$

where:

a = linear dimension

Re = Reynolds number

The rate of a process taking place in the external diffusion region may be expressed in terms of the rate of diffusion (convective) transfer to the external surface, subject to (5.2):

$$w_{rA} = w_{\text{conv},A} = -(1/S)(dn_A/d\tau) \approx \beta_A C_{A,g} \quad (5.4)$$

where:

S = external surface of the catalyst grain

β_A = individual mass transfer coefficient which is a function of the diffusivity of component A and the thickness of the boundary diffusion layer

When the diffusion involves several gases, Eq. (5.4) holds for the slowest component.

As is seen from Eq. (5.4), the rate of the process taking place in the external diffusion region is formally described by a first-order equation (it is directly proportional to the concentration of the gaseous reactant), irrespective of the mechanism by which the catalytic reaction proceeds, and the true kinetic relationships.

The activation energy of a heterogeneous catalytic process in this region is formally determined by the temperature dependence of the diffusion coefficients.* Because this dependence is a weak one, the activation energy

* The "apparent" activation energy of a catalytic reaction is meant here.

is very small or even equal to zero. Therefore when the temperature of the process is raised, the rate of reaction rises faster than the rate of diffusion. In consequence, the rate of diffusion becomes a controlling factor in the region of high temperatures.

The implementation of a catalytic process in the external diffusion region may be accompanied by some untoward phenomena. Since heat transfer is similar to mass transfer, the coefficients of heat transfer from the surface of the catalyst grain into the bulk gas are small under conditions of slow diffusion. In the case of exothermic reactions, this might lead to an excessive heat build-up in the catalyst, and this is an undesirable development because reversible reactions might take place — the heat build-up might cause the position of equilibrium to be shifted in the backward direction. In the case of series reactions, a slow-down in the transport of the intermediates results in that they stay at the surface for a longer time and promote side reactions with a concomitant impairment in specificity.

When a reaction moves into the external diffusion region, its rate is markedly reduced in comparison with what it is when the reaction takes place in the kinetic region. For example, the rate of ammonia oxidation may fall by 99% and that of SO_2 oxidation by 2.5–47% as compared with their rates in the kinetic region.

The transition of a process from the external diffusion into the kinetic region can be favoured by a reduced process temperature, an increased linear velocity of the gas stream, more intensive agitation, a reduced pressure, and a reduced size of catalyst grains.

The effect of mass transfer in the pores. A catalytic reaction takes place mainly at the surface of the pores in the catalyst grain because the internal surface of the catalyst is by several orders of magnitude greater than its external surface. Therefore, the manner in which the reactants are transported into the pores of the catalyst may markedly affect the course of the chemical reaction.

If the diffusion in the pores of the catalyst grain proceeds at a faster rate than the chemical reaction, all of the accessible surface of the catalyst will obviously take part in the reaction because the reactants are able to reach the internal surface before they react with each other. In the circumstances, there is a steady diffusion flow despite the fact that the difference in concentration between the outer and inner parts of the catalyst grain is small. This diffusion flow moves the reacting molecules inside the grains and withdraws the products. With slow chemical reactions, practically all of the internal surface of the catalyst grain serves a useful purpose.

These slow reactions contrast with fast reactions over a very active catalyst — now the reactants are converted to products well before they

have a chance to enter pores. An abrupt concentration gradient is produced at the external surface of the grain, and the reacting molecules rapidly diffuse to a small depth into the pores while the product molecules diffuse as rapidly outside. As a result, almost all of the reaction occurs at the external surface of the catalyst grain and the internal surface of the porous structure remains unused.

Thus, the extent to which the internal surface of the catalyst grain is utilized in a reaction depends on the relative rate of the diffusion into the pores and the chemical process, both of which proceed concurrently.

The utilization of the internal surface of the catalyst grain. How well the internal surface of the catalyst grain is utilized depends on the operating conditions (such as temperature, pressure, and others) which affect the rate constant and the diffusion coefficient. For example, in the catalytic synthesis of ammonia over a promoted iron catalyst (500 °C, 30 MPa), the utilization of the internal surface of the catalyst is 5.4%. In the oxidation of sulphur dioxide over a vanadium catalyst (450 °C, 0.98 MPa, 8 vol.% SO₂, 12 vol.% O₂), the figure is 71%.

Quantitatively, the utilization of the internal surface of a catalyst may be evaluated in terms of the *effectiveness factor* ϵ . It is defined as the ratio between the average rate of consumption of a reactant in the pores of a catalyst and the maximum rate of consumption which would result if there were no slow-down effect from pore diffusion*

Let us derive an equation for the effectiveness factor when the catalyst has straight cylindrical pores of radius R and length L (Fig. 5.3a) and the reaction that takes place at their surface is a 1st-order reaction whose rate equation takes the form

$$w_{rA} = -(1/S)(dn_A/d\tau) = k_s C_A \quad (5.5)$$

where:

S = catalyst surface area

k_s = rate constant of the 1st-order surface reaction

Since the concentration of reactant A decreases on moving farther into a pore owing to the slow-down effect of pore diffusion, it follows that the reaction rate must be different at the mouth of, and the exit from, the pore. The rate of reaction will be a maximum when the reactant concentration along the pore is the same as it is at the external surface, $C_{A,s}$:

$$-(dn_A/d\tau)_{\max} = k_s S C_{A,s} \quad (5.6)$$

* There is a different definition: The effectiveness factor is the ratio of actual reaction rate per unit mass of catalyst to the rate that would result if the complete internal surface of the catalyst were available for the reaction (R.H. Perry & C.H. Chilton, *Chemical Engineers' Handbook*, 5th Ed., p. 4-9). — *Translator's note.*

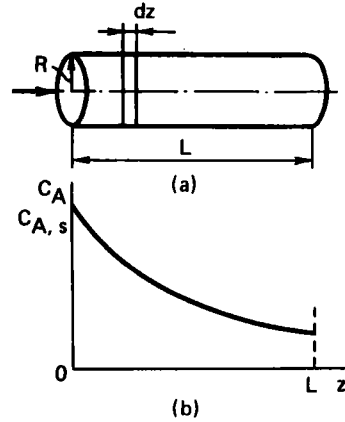


Fig. 5.3 (a) A straight cylindrical pore in a catalyst grain and (b) reactant concentration distribution along pore length

Here, S is the internal surface area of a cylindrical pore, defined as

$$S = 2\pi RL \quad (5.7)$$

In view of Eq. (5.7),

$$-(dn_A/d\tau)_{\max} = 2\pi RLk_s C_{A,s} \quad (5.8)$$

The actual rate of reaction in terms of reactant A in the face of the slow-down caused by pore diffusion cannot exceed the rate at which reactant A enters the mouth of the pore due to molecular diffusion:

$$-(dn_A/d\tau)_{av} = D\pi R^2(dC_A/dz)_{z=0} \quad (5.9)$$

where z is the distance along the pore.

In view of Eqs. (5.8) and (5.9), the effectiveness factor may be written as

$$\varepsilon = \frac{D\pi R^2(dC_A/dz)_{z=0}}{2\pi RLk_s C_{A,s}} = \frac{DR(dC_A/dz)_{z=0}}{2k_s LC_{A,s}} \quad (5.10)$$

In order to find the concentration gradient at the mouth of the pore, $(dC_A/dz)_{z=0}$, we need to evaluate the function $C_A(z)$. For this purpose we write a material balance over an infinitesimal volume cut out in a pore by two parallel planes spaced dz apart (Fig. 5.3a). Reactant A is delivered to this volume solely by diffusion

$$-\pi R^2 D(dC_A/dz)_z \quad (5.11)$$

Reactant A is expended likewise by diffusion in the section $z + dz$

$$-\pi R^2 D(dC_A/dz)_{z+dz} = -\pi R^2 D[dC_A/dz + (d^2C_A/dz^2)dz] \quad (5.12)$$

and due to the surface chemical reaction:

$$2\pi R dz k_s C_A \quad (5.13)$$

Under steady state conditions, the algebraic sum of the streams described by Eqs. (5.11), (5.12) and (5.13) is zero:

$$\pi R^2 D (d^2 C_A / dz^2) dz - 2\pi R dz k_s C_A = 0 \quad (5.14)$$

or

$$d^2 C_A / dz^2 - (2k_s / RD) C_A = 0 \quad (5.15)$$

On designating

$$2k_s / RD = m^2 \quad (5.16)$$

we may write

$$C_A'' - m^2 C_A = 0 \quad (5.17)$$

which is a homogeneous 2nd-order differential equation. We will seek its solution subject to the following boundary conditions:

$$(1) \text{ at } z = 0, \quad C_A = C_{A,s} \quad (5.18)$$

$$(2) \text{ at } z = L, \quad (dC_A / dz)_L = 0 \quad (5.19)$$

that is, at the bottom of the pore the diffusion stream is non-existent (Fig. 5.3b).

We seek the particular solution of Eq. (5.17) in the form

$$C_A = \exp(Az)$$

Then

$$C_A' = A \exp(Az)$$

and

$$C_A'' = A^2 \exp(Az)$$

so Eq. (5.17) takes the form

$$A^2 \exp(Az) - m^2 \exp(Az) = 0$$

Hence,

$$A = \pm m$$

Therefore, the particular solutions of Eq. (5.17) are

$$C_A = \exp(mz)$$

and

$$C_A = \exp(-mz)$$

and the general solution of the equation is their linear combination

$$C_A = M_1 \exp(mz) + M_2 \exp(-mz)$$

The constants of integration, M_1 and M_2 , can be found from the boundary conditions defined in (5.18) and (5.19).

It follows from (5.18) that at $z = 0$,

$$C_{A,s} = M_1 + M_2$$

or

$$M_2 = C_{A,s} - M_1$$

It follows from (5.19) that at $z = L$,

$$(dC_A/dz)_{z=L} = M_1 m \exp(mL) - M_2 m \exp(-mL) = 0$$

or, subject to Eq. (5.21),

$$M_1 \exp(mL) - C_{A,s} \exp(-mL) + M_1 \exp(-mL) = 0$$

Hence,

$$M_1 = C_{A,s} \frac{\exp(-mL)}{\exp(mL) + \exp(-mL)} = C_{A,s} \frac{\exp(-mL)}{2 \cosh(mL)} \quad (5.22)$$

where

$$\cosh(mL) = [\exp(mL) + \exp(-mL)]/2$$

Thus, the distribution of C_A along the pore's length, that is, $C_A(z)$, has the form

$$\begin{aligned} C_A &= C_{A,s} \frac{\exp(-mL) \exp(mz)}{2 \cosh(mL)} + C_{A,s} \frac{\exp(mL) \exp(-mz)}{2 \cosh(mL)} \\ &= C_{A,s} \frac{\cosh[m(L-z)]}{\cosh(mL)} \end{aligned} \quad (5.23)$$

Now it is an easy matter to find the concentration gradient at the mouth of the pore

$$(dC_A/dz)_{z=0} = -\frac{C_{A,s} m}{\cosh(mL)} \sinh(mL) = -m C_{A,s} \tanh(mL) \quad (5.24)$$

On substituting Eq. (5.24) into Eq. (5.10), we obtain subject to Eq. (5.16)

$$\varepsilon = \frac{DRmC_{A,s} \tanh(mL)}{2k_s LC_{A,s}} = \frac{\tanh(mL)}{mL} \quad (5.25)$$

The quantity

$$mL = L(2k_s/RD)^{1/2} = h_1 \quad (5.26)$$

is called the *Thiele modulus* (the subscript '1' indicates that it is derived for a 1st-order reaction).

Thus,

$$\varepsilon = (1/h_1) \tanh h_1 \quad (5.27)$$

The plot of the hyperbolic trigonometric function $\tanh h_1$ has the shape shown in Fig. 5.4. As is seen, when $h_1 < 0.5$, then $\tanh h_1 \cong h_1$. In consequence, the effectiveness factor at low values of h_1 is practically equal to

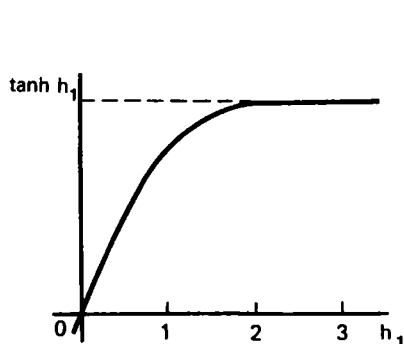


Fig. 5.4 Plot of the hyperbolic trigonometric function $\tanh h_1$

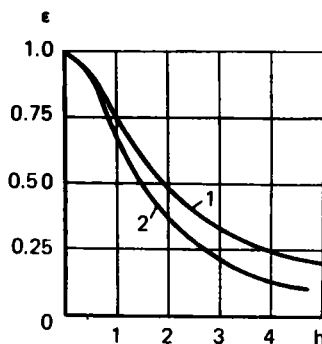


Fig. 5.5 Catalyst effectiveness factor ε as a function of the Thiele modulus for (1) a 1st-order and (2) a 2nd-order reaction

unity. This is the case when a catalyst has short, wide pores and the rate constant of the surface reaction is small in comparison with the diffusion coefficient.

At $h_1 > 4$, it may be assumed that $\tanh h_1 \cong 1$. Then an increase in h_1 brings on a decrease in ε . In consequence, the effectiveness of the catalyst is low if it has long, narrow pores, and the rate constant of the surface reaction is high (say, at elevated temperatures). If $h_1 \gg 1$, then ε tends to zero.

When the value of ε is known, the rate equation is multiplied by the effectiveness factor, and the reactor design is then carried out on the basis of the rate equation thus derived, in which the reactant concentration is $C_{A,s}$ that is established through the adsorption of reactant A on the external surface of the catalyst.

The effectiveness factor may be derived for reactions of other than the 1st order as well. Thus, for a 2nd-order reaction

$$\varepsilon = (1/h_2)(2/3)^{1/2} \quad (5.28)$$

where

$$h_2 = L(2k_s C_{A,s}/RD)^{1/2} \quad (5.29)$$

A plot of the effectiveness factor ε as a function of the Thiele modulus for a 1st- and a 2nd-order reaction is shown in Fig. 5.5.

The adsorption step. The step during which the reactants are adsorbed on the surface of the catalyst is decisive for the entire course of a heterogeneous catalytic process. The manner of adsorption markedly affects the form of the rate equations that are used to design a catalytic reactor. This warrants a closer examination of the adsorption step.

With physical adsorption, a state of equilibrium between the adsorbed particles and the particles remaining in the gas phase is established rather

rapidly. In this state the rate of adsorption is equal to that of desorption. There is a body of opinion that physical adsorption is brought on by the same forces (van der Waals forces) of molecular interaction that are responsible for the condensation of vapours. The heat of physical adsorption is small, being close to that of condensation and amounting in most cases to $10\text{--}40\text{ kJ mol}^{-1}$. As a rule, physical adsorption plays an important part in cases where the temperature of the gas falls below critical, that is, when the gas exists as a vapour.

Chemical adsorption may occur at temperatures lying both above and below the critical temperature of the adsorbent. What sets it apart from physical adsorption is its high specificity — it depends on the chemical nature of the adsorbent and the adsorbate. The heat of chemical adsorption is close in value to the heats of chemical reactions. Chemically adsorbed substances are far more difficult to remove from the surface of the adsorbent than those adsorbed physically, and the desorption may be accompanied by chemical reactions. For example, the thermal desorption of oxygen from carbon (oxygen is strongly chemisorbed on carbon) produces a mixture of CO and CO₂ rather than oxygen.

Chemical adsorption is infrequently a relatively slow process which proceeds at a rate determined by the presence of an activation barrier (hence the name 'activated adsorption'). Chemical adsorption may consist of two steps: at first, the rapid physical adsorption of the gas takes place, then the gas slowly reacts with the surface of the solid.

At low temperatures the rate of chemisorption is low, and only physical adsorption practically takes place. Conversely, physical adsorption is nearly non-existent at high temperatures, so that only chemisorption occurs.

The rate of heterogeneous catalytic processes is proportional to the surface concentrations of the adsorbed molecules. Because it may be deemed in many practical cases that an adsorption-desorption equilibrium exists at the surface of the catalyst, the surface concentrations of the reactants may be evaluated from the equilibrium distribution of the adsorbate molecules between the surface of the solid and the gas phase. This distribution is a function of the pressure, temperature and nature of the adsorbent and adsorbate and the surface area of the adsorbent. It is customary to evaluate the equilibrium distribution from adsorption isotherms which show how the quantity of adsorbate depends on the equilibrium partial pressure of a given gas at a constant temperature.

Several adsorption isotherms have been proposed to date. We will dwell on that due to Langmuir and known as the *Langmuir adsorption isotherm*. It is derived on the basis of several assumptions, namely:

(1) The adsorbed particles are associated with definite active sites on the surface of the adsorbent.

(2) Only one adsorbate particle can attach itself to each site.

(3) The energy of the adsorbed particles is the same at all sites on the surface and independent of the presence of other adsorbed particles at adjacent sites.

Unless the above assumptions are adopted, much more complex equations have to be developed.

The Langmuir adsorption isotherm can be deduced from the equality between the rates of adsorption and desorption at equilibrium. Let component A be the only adsorbate whose equilibrium pressure in the gas phase is p_A . There is, on the surface, a definite total number N_{tot} of adsorption sites (or centres) some of which, N_A , are occupied by the adsorbed molecules and the remainder, $N' = N_{tot} - N_A$, are left uncovered. The rate of desorption (evaporation) is assumed to be proportional to N_A and equal to

$$w_{des} = k_1 N_A \quad (5.30)$$

where k_1 is the rate constant for desorption. The rate of adsorption (condensation) is proportional to the number of uncovered sites, N' , and the pressure of the gas:

$$w_{ads} = k_2 p_A N' = k_2 p_A (N_{tot} - N_A) \quad (5.31)$$

where k_2 is the rate constant for adsorption. At equilibrium, $w_{ads} = w_{des}$, and

$$k_1 N_A = k_2 p_A (N_{tot} - N_A) \quad (5.32)$$

Let us introduce the adsorption factor, b_A , defined as the ratio of the rates for adsorption and desorption

$$b_A = k_2 / k_1 \quad (5.33)$$

It follows from Eq. (5.32) that

$$N_A = N_{tot} \frac{b_A p_A}{1 + b_A p_A} \quad (5.34)$$

Let the ratio of the number of sites covered to the total number of adsorption sites (that is, the fraction of surface covered) be designated as

$$\theta_A = N_A / N_{tot} \quad (5.35)$$

Then the Langmuir adsorption isotherm may be written as

$$\theta_A = \frac{b_A p_A}{1 + b_A p_A} \quad (5.36)$$

Analysis of Eqs. (5.34) and (5.36) shows that at low pressure the quantity of adsorbed gas is proportional to its pressure

$$N_A \approx N_{tot} b_A p_A \quad (5.37)$$

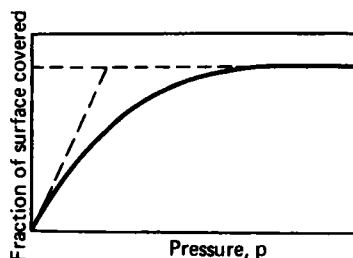


Fig. 5.6 Langmuir adsorption isotherm

and

$$\theta \approx b_A p_A \quad (5.38)$$

At high pressures, the adsorbate tends to cover all of the surface, and θ tends to unity (Fig. 5.6).

For adsorption of an i th component from a mixture of n gases, the above reasoning leads to the following equation

$$N_i = N_{tot} \frac{b_i p_i}{1 + \sum_{j=1}^n b_j p_j} \quad (5.39)$$

or

$$\theta_i = \frac{b_i p_i}{1 + \sum_{j=1}^n b_j p_j} \quad (5.40)$$

where:

b_j = adsorption factor for reactant J

N_j = number of adsorption sites covered by the molecules of reactant J

p_j = partial pressure of reactant J

θ_j = fraction of surface covered by adsorbed reactant J

The adsorption factor b_A is a function of temperature and the heat of adsorption (the energy of interaction between the adsorbate and the surface) which, within the framework of the Langmuir adsorption isotherm, is taken to be constant and independent of the fraction of surface covered:

$$b_A = b_{A,0} \exp(Q_A/RT) \quad (5.41)$$

where:

$b_{A,0}$ = frequency factor

Q_A = heat of adsorption for component A

The effect of adsorption on the kinetics of heterogeneous catalysis. For the chemical engineer to be able to design a catalytic reactor, he needs to

know the concrete form of the rate equation, that is the manner in which the rate of the process depends on the concentration of the participants, temperature, etc. By analogy with homogeneous systems, the rate of a catalytic reaction depends on the surface concentrations of the adsorbed particles. In practice, one knows the volume rather than surface concentrations of the components in the gas phase or their partial pressures. Therefore, it is customary to write the rate equations for heterogeneous catalytic reactions in a form relating the rate to the concentration of the reactants in the gas phase (the partial pressures).

Rate equations are not simple to derive. It is not always possible to consider rigorously all the chemical and physical factors involved, and simplifying assumptions have to be made. The most commonly used kinetic model is the one due to Langmuir and Hinselwood. Within the framework of this model it is assumed that the reacting components are present in their equilibrium surface concentrations with respect to their volume concentrations and the molecules in the adsorbed layer are sufficiently mobile and can experience numerous collisions before they are desorbed.

Under the above assumptions, the adsorption equilibrium is described by the Langmuir adsorption isotherm and the reaction rate is subject to the surface action law (which is analogous to the mass action law applicable to chemical processes that take place at the surface of a solid).

As an example, let us derive rate equations for irreversible monomolecular and bimolecular reactions.

Example 5.1. In accord with the mass action law, the rate of the monomolecular surface reaction



is proportional to the number of adsorbed particles:

$$w_{rA} = -(1/S)(dn_A/d\tau) = k\nu_A \quad (5.42)$$

where

$$\nu_A = N_A/S$$

is the number of adsorbed molecules per unit surface. (Accordingly,

$$\sigma = N_{tot}/S$$

is the total number of adsorption sites per unit surface.) In view of Eq. (5.39),

$$w_{rA} = -(1/S)(dn_A/d\tau) = k\sigma \left(\frac{b_A p_A}{1 + b_A p_A + b_R p_R + b_M p_M} \right) \quad (5.43)$$

If products R and M are only slightly adsorbed, Eq. (5.43) is simplified:

$$w_{rA} = k\sigma b_A \frac{p_A}{1 + b_A p_A} = k' \frac{p_A}{1 + b_A p_A} \quad (5.44)$$

where

$$k' = k\sigma b_A$$

Thus, the rate of a monomolecular reaction is described by an equation similar to the Langmuir isotherm; at low pressures of component A the reaction rate is proportional to p_A while at high pressures it tends to a limiting value, $k\sigma$.

From an analysis of the temperature dependence of the rate constant we may form an idea about the true and apparent activation energies of catalytic reactions. The temperature dependence of k' has the form

$$k' = k'_0 \exp(-E'/RT) = k_0 \exp(-E/RT) \sigma b_{A,0} \exp(Q_A/RT) \quad (5.45)$$

where:

E' = apparent (experimentally found) activation energy of a catalytic reaction

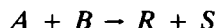
E = true activation energy of a surface reaction including the adsorbed particles

On neglecting the weak temperature dependence of σ and $b_{A,0}$ we get

$$d \ln k' / dT = E' / RT^2 = (E - Q_A) / RT^2 \quad (5.46)$$

Hence it follows that the true activation energy is greater than the apparent activation energy by an amount equal to the heat of adsorption.

Example 5.2. For the bimolecular surface reaction



the reaction rate is

$$w_{rA} = -(1/S)(dn_A/d\tau) = k\nu_A\nu_B \quad (5.47)$$

Using Eq. (5.39) in order to find ν_A and ν_B for adsorption from a binary mixture, we get

$$w_{rA} = k\sigma \left[\frac{b_A b_B p_A p_B}{(1 + b_A p_A + b_B p_B + b_R p_R + b_S p_S)^2} \right] \quad (5.48)$$

The rate equations derived in Examples 5.1 and 5.2 hold for two very simple surface reactions, and their derivation was based on quite a number of simplifying assumptions. Yet, this approach yields equations which

describe fairly accurately a number of catalytic processes (such as the dehydrogenation and dehydration of organic compounds). When allowance is made for the dependence of surface bond energy on the fraction of surface covered by chemisorbed particles, rate equations can be deduced for a number of commercial processes, such as ammonia synthesis, carbon monoxide conversion, and SO_2 oxidation. When deriving rate equations for commercial chemical processes it is likewise important to consider that they proceed via several steps, that the reaction mixture affects the composition and properties of the catalyst, etc.

Part Two

CHEMICAL REACTORS

Chapter Six

GENERAL REMARKS

The implementation of any industrial chemical process involves the use of several pieces of equipment interconnected into a chemical processing unit or plant. The key pieces in the overall plant layout are chemical reactors.

6.1 Classification and Operating Conditions of Chemical Reactors

Chemical reactors intended for use in different processes differ in design, size and geometry. For all the differences, however, they may be classed on the basis of a number of common features so that reactor data can be presented in a systematic way, the reactors themselves can be described mathematically, and a judicious choice of design procedures can be made.

Most often chemical reactors and their operating conditions are classified according to:

- (1) The flow pattern of the reaction mixture.
- (2) Conditions of heat transfer in the reactor.
- (3) The phase make-up of the reaction mixture.
- (4) The mode of operation.
- (5) Variations in the process variables with time.
- (6) Constructional features.

Classification according to the flow pattern of the reaction mixture. In this respect, reactors may be classed into the stirred-tank type and the tubular type.

A *stirred-tank reactor* is essentially a tank whose contents (the reaction mixture) are agitated by a mechanical stirrer or a recirculating pump.

A *tubular reactor* is essentially a conduit (a tube or a pipe) in which the reaction progresses as the reactants move down the conduit. In a tubular reactor, mixing is of local character and is mainly due to a non-uniform distribution of stream velocity, velocity fluctuations, and eddies.

In the theory of chemical reactors it is customary first to consider two ideal cases of flow pattern — *perfect or complete mixing* and the *plug flow*, and two extreme or ideal types of reactor — the ideal stirred-tank type and the ideal, or plug flow, tubular type *.

In an *ideal stirred-tank* (or *well-stirred tank*) reactor, all the reaction variables are completely the same at any point throughout the reactor's volume.

In an *ideal (or plug flow) tubular reactor*, any quantity of reactants and products moves down the reactor in the form of plugs so that a distinct distribution of individual concentrations, temperature and other variables is established over the reactor's length (in the reactor volume) as dictated by the nature of the reaction and of the accompanying physical phenomena **.

Real reactors approach either the ideal stirred-tank type or the ideal tubular type to a varying degree. When suitably corrected for the deviations from the ideal, these models may be used as starting points in the analysis and design of real reactors.

Classification according to conditions of heat transfer. The chemical reactions taking place in a reactor are accompanied by the release or absorption of heat and the associated physical processes (dissolution, crystallization, evaporation, etc.). As an amount of heat is released or absorbed, the temperature in the reactor changes, and a temperature difference is established between the reactor and the surroundings. Given certain conditions, there appear temperature gradients inside the vessel. The difference in temperature, ΔT , is the driving force of heat transfer.

When no heat is transferred between the reactor and the surroundings, we have an *adiabatic reactor*. Here all of the heat released or absorbed in a chemical conversion is used up in 'internal' heat transfer — the reaction mixture is either heated or cooled.

When heat transfer to or from the surroundings maintains a constant temperature inside the vessel, we have an *isothermal reactor*. Heat transfer fully equalizes the release and absorption of heat at any point inside the reactor.

When the heat evolved or taken up by the chemical reaction is partly balanced by the heat exchanged with the surroundings and partly causes a

* They also go by other names such as the perfect stirred-tank type, the well-stirred tank type, the perfectly or well mixed tank type, and as the perfect tubular type, the plug-flow tubular type. Since the plug flow condition may occur only in a tubular reactor, the term 'plug-flow' refers to an ideal tubular reactor. — *Translator's note.*

** Importantly, no interchange of material occurs between a plug and the material either leading or following the plugs. — *Translator's note.*

change in the temperature of the reaction mixture, we have a *transition-type* or *heat-regulated reactor*.

There is also the *autothermal type of reactor* in which the desired temperature is maintained solely by the heat of reaction and no heat comes from external sources. It is generally sought that reactors, especially those in tonnage chemical plants, be of the autothermal type.

Classification according to the phase make-up of the feed. Reactors for homogeneous reactions may be gas-phase and liquid-phase types. Reactors for heterogeneous reactions may be gas-liquid, gas-solid, liquid-solid, etc. types. Reactors for heterogeneous catalytic reactions constitute a separate group.

Classification according to the mode of operation. This refers to how the reactants are fed to and the products are discharged from a reactor. Thus there are batch reactors, semibatch reactors, and continuous reactors.

In a *batch reactor*, the individual steps occur consecutively, at different times. All reactants are fed into the tank prior to the start of the reaction, and the product mixture is discharged after the process has been carried to completion. The duration of the process may be measured directly because the reaction time and the residence time (that is, the time during which the reactants are retained in the reaction vessel) are the same. The process variables of a batch reactor vary with time.

One operating cycle of a batch reactor has to be separated from the next by auxiliary operations during which a fresh amount of reactants (or feed) is admitted to the vessel and the products of the previous cycle are discharged. Because these auxiliary operations do not yield any additional amount of products, they reduce the throughput of a batch reactor.

In a *continuous reactor*, the individual steps of the process (admission of the reactants, the chemical reaction, and discharge of the products) proceed in parallel (concurrently), and so there is no time wasted on non-productive operations. This is the reason why in present-day tonnage chemical processes where the plant is expected to operate at a high throughput most chemical reactions are effected in continuous reactors.

The residence time of the individual particles of the reactant stream in a continuous reactor is, in the general case, a random quantity. Because the reaction time has a direct bearing on the degree of conversion, it is of necessity different for particles differing in residence time. The mean degree of conversion depends on the residence time distribution function of the individual particles, dependent in turn on the nature of mixing and the flow pattern in the reactor, and is different for each type of flow-pattern.

A *semi-batch* (or *semicontinuous*) reactor is that in which one of the reactants enters the vessel continuously and the other, intermittently. In

some cases, the reactants enter a reactor intermittently and the reaction products are discharged continuously, or the other way around.

Classification according to variations in the process variables with time. In this respect reactors may be classified into those operating under steady-state and unsteady-state conditions.

Let us select an arbitrary point inside a chemical reactor. The reactor will be said to operate under *steady-state conditions* if the concentrations of the reactants and products, reaction temperature, reaction rate and other process variables remain unchanged with time (that is, they are time-invariant). Under steady-state conditions, the variables of the stream leaving the reactor are independent of time. As a rule, the time-invariance of the exit variables is secured through the time-invariance of the inlet variables.

If the process variables at some arbitrary point inside a reactor do change with time, the reactor is said to be operating under *unsteady-state conditions*. This is the more common case of the two. Operation under steady-state conditions is possible in continuous reactors, but even they are operating under unsteady-state conditions at start-up and shut-down. All batch reactors operate under unsteady-state conditions.

In reactors operating under unsteady-state conditions, there may be a positive or a negative accumulation of material or energy. For example, in a batch reactor there is a positive accumulation of the reaction products and a negative accumulation (or loss) of the reactants. Should an exothermic reaction take place in such a reactor with no heat transfer to the surroundings, there will be an accumulation of heat (energy), and the temperature of the reaction mixture will rise.

Continuous reactors operating under steady-state conditions are simpler to model (they can be described by simpler equations); the processes that are effected in them are easier to automate.

Quite naturally, operation under unsteady-state conditions complicates both the description of the reactor and the control of its operation. In many cases, however, the process variables of reactors operating under unsteady-state conditions are easier and simpler to optimize.

Classification according to constructional features. Chemical reactors differ in quite a number of features that affect their design and construction. Thus, there are reactors which are basically tanks (autoclaves, chambers, vertical or horizontal cylindrical converters), columns or towers (packed or tray-type), fixed-bed, moving-bed, and fluidized-bed catalytic reactors, shelf-type reactors, heat-exchanger type reactors, shaft-type reactors (shaft, shelf, chamber, and rotating tubular kilns, ovens or furnaces), etc.

6.2 Mathematical Modelling of Chemical Reactors

Chemical reactor design is based on the modelling of reactors and of the reactions that take place in them. Modelling is a method of study by which the object or process of interest is replaced with its model on which all the necessary tests are carried out and the results are extended to the prototype. A model may be a scaled-down or a scaled-up replica of an actual plant or process. On the other hand, a model may be an ordered set of mathematical structures that is, equations, inequalities, charts, and tables that give the investigator an idea about the prototype. This is a mathematical model of a prototype.

A mathematical model is a simplified image of the process that takes place in a reactor. It retains the most essential properties of the actual process and presents them in mathematical form. Depending on the objective sought, a mathematical model may involve a varying number of properties of the prototype, and so it may be wide or narrow.

The mathematical model of a chemical reactor must be, on the one hand, sufficiently simple and give an easy-to-grasp and clear idea about all the qualitative aspects of the phenomenon of interest (it is only then that a form of 'physical control' may obviously be retained over the model). On the other hand, it must be sufficiently accurate in bringing out the quantitative aspects of the process. These are conflicting requirements because unless a detailed and in-depth study has been undertaken, it is not always clear which factors or aspects are most essential. Therefore, a mathematical model is not at all simple to develop.

When developing a mathematical model, resort should preferably be made to the hierarchical approach to a reactor as a complex system *. Basically, the hierarchical approach consists in that a complex system is treated as an assemblage of subsystems interrelated in a definite manner. The subsystems of a lower rank perform all the functions falling within the terms of reference of a subsystem belonging to the next higher rank.

A reactor or a reaction unit is a complex piece of plant, organized in a multistep structure. Accordingly, the respective mathematical model is built from those of the subordinate steps or stages and involves relationships connecting the lower ranks to the next higher ranks or levels. Step-wise study of a process enables the designer to progress towards a higher-level model by including in it the models belonging to the previous lower level. The preceding analysis of the lower-level models substantially simplifies analysis of the process as a whole. Also, the hierarchical ap-

* Hierarchy is a manner of organizing data, things, etc. into ranks, each rank having a higher precedence than those below it.

proach takes proper account of the relationships between the various levels of the entire system.

Any chemical process taking place in a reactor may be thought of as consisting of the following levels (counted from bottom upwards).

The *molecular level* refers to intermolecular processes that take place over distances comparable with the size of the reacting molecules and are subject above all to the laws of chemical kinetics. An analysis of this level relies on stoichiometry which establishes quantitative relationships between the consumption of the various reactants and the formation of reaction products and the laws of chemical equilibrium.

The *small-volume level* refers to a macroscopic element of the reaction space, which may geometrically be a sphere or a cylinder whose cross-sectional area is a few square millimetres or centimetres. This macroscopic element may be a catalyst grain, a gas bubble, a packing element in a packed tower, etc. The relations and mechanisms unravelled at the previous lower level must now be supplemented with those of heat and mass transfer.

The *reaction-zone level* refers to a static assemblage of the small-volume elements studied at the previous lower level. This may be a catalyst bed, the packing bed of a column, a fluidized bed, etc. At this level it is important to consider the effects associated with the flow pattern. In some cases (such as when homogeneous reactions are involved), the investigator may pass to this level directly from the molecular level, thus leaving out the small-volume level.

The *reactor level* refers to the configuration, interrelation and relative position of the various zones in a reactor, say, several catalyst beds separated by heat exchangers in a multibed reactor.

The *plant level* refers to the relationships between the various pieces of equipment that make up the complete plant in question.

The mathematical models of the higher hierarchical levels usually include several equations, both of the finite-difference type which do not contain any differentiation operators, and differential equations (both ordinary and partial). Therefore the mathematical model of a reactor is in the general case a rather complex system of equations, and the computations based on them should preferably be done on a computer. When properly built, the model of a chemical reactor or of a chemical process enables the designer to develop a computer control system for the reactor or process as a whole as well.

On the other hand, when describing the chemical process as it proceeds at the lower hierarchical levels, the designer may often use relatively simple mathematical models so that the physical nature of the phenomena in question are also considered.

Any mathematical description of a chemical reactor heavily relies on

balance equations which express the general laws of conservation of mass and energy. A mathematical model of a chemical reactor will always include material and heat balance equations.

A material balance (one or several) may be written on one or several components taking part in a reaction (they may be reactants and/or products) so that it reflects all the changes that this component undergoes. When a simple reaction takes place in a reactor, it is customary to write one material balance on any one reactant or product. When a complex reaction is involved, the mathematical description will usually include several material balance equations on several substances each of which participates in at least one of the simple reactions that make up the overall complex reaction.

Material balances may be written on an element of volume ΔV and over an element of time $\Delta \tau$. The volume element ΔV is one selected inside a reactor so that variations in the concentration and temperature distributions within the element may be neglected. The volume element is stationary with respect to the reactor and does not move along with the reaction stream. In the general case, ΔV is infinitesimal along any dimension, although in some cases (such as with an ideal well-stirred reactor) it may be deemed equal to the entire reactor volume because the concentrations and temperatures are now distributed uniformly throughout the reactor.

The element of time $\Delta \tau$ is that during which we may neglect changes in the concentrations and temperatures inside the volume element ΔV . The time element is infinitesimal when the reactor is operating under unsteady-state conditions and may be chosen of any magnitude for operation under steady-state conditions (equal to, say, 1 hr or 1 min).

Let us see what a material balance looks like.

The material balance on substance J gives an account of all forms of supply and discharge of this component within the selected volume element ΔV and during the selected element of time $\Delta \tau$:

$$n_{J,in} - n_{J,out} \pm n_{J,r} = n_{J,acc} \quad (6.1)$$

where:

$n_{J,in}$ = quantity of substance J entering the volume element ΔV with the reactant stream during the element of time $\Delta \tau$

$n_{J,out}$ = quantity of substance J leaving ΔV during $\Delta \tau$ with the exit stream

$n_{J,r}$ = quantity of substance J used up in the chemical reaction (or formed by the chemical reaction) in ΔV during $\Delta \tau$

$n_{J,acc}$ = quantity of substance J accumulated in ΔV during $\Delta \tau$

A similar procedure applies to heat balances. Taking an element of time $\Delta \tau$, one considers all the heat streams entering, leaving or forming in an element of volume ΔV . Their algebraic sum is equal to the quantity of heat

accumulated (or expended) in ΔV during $\Delta\tau$:

$$Q_{in} - Q_{out} \pm Q_r \pm Q_t = Q_{acc} \quad (6.2)$$

where:

Q_{in} = heat content of the substances entering ΔV during $\Delta\tau$

Q_{out} = heat content of the substances leaving ΔV during $\Delta\tau$

Q_r = quantity of heat released or absorbed during the chemical reaction in ΔV during $\Delta\tau$

Q_t = quantity of heat transferred between ΔV and the surroundings during $\Delta\tau$

Q_{acc} = quantity of heat accumulated in ΔV during $\Delta\tau$

Chapter Seven

REACTORS WITH AN IDEAL FLOW PATTERN

As already noted, a study of chemical reactors as complex systems should be commenced, within the framework of the hierarchical approach, by first building models for the individual subsystems at the lower levels and then passing on to the higher levels.

Let us begin by considering models applicable to homogeneous, isothermal reactors with ideal flow patterns — the ideal stirred-tank reactor and the ideal (or plug-flow) tubular reactor. When building mathematical models for these reactors, it will suffice, to a first approximation, to consider the mechanisms by which the participating species interact at the microscopic level (stoichiometry, equilibrium, and microkinetics), and also the effects associated with a given flow pattern.

7.1 The Ideal Stirred-Tank Reactor

Several simplifying assumptions are made in building a model for the ideal stirred-tank or well-stirred tank reactor. Firstly, it is assumed that vigorous agitation establishes absolutely identical conditions throughout the reactor; that is, the concentrations of the reactants and products, the degree of conversion of the reactants, the reaction temperature and rate, etc. are the same at any point in the reactor volume. This means that at some instant, τ_i , the following conditions are satisfied at all points inside the reactor (Fig. 7.1):

$$\begin{aligned} C_j(x_1, y_1, z_1, \tau_i) &= C_j(x_2, y_2, z_2, \tau_i) = \dots \\ &= C_j(x_N, y_N, z_N, \tau_i) \end{aligned} \quad (7.1)$$

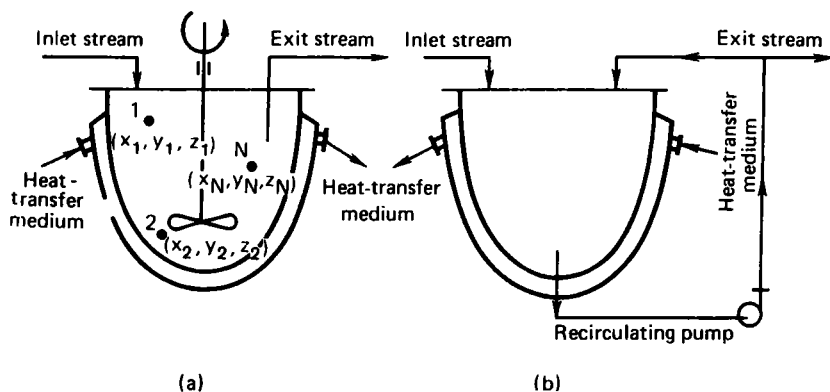


Fig. 7.1 Perfectly mixed (well-stirred) reactors: *a*, with a mechanical stirrer; *b*, with a recirculating pump of high recirculating factor

$$(\partial C_J / \partial x)_{\tau_i} = 0, (\partial C_J / \partial y)_{\tau_i} = 0, (\partial C_J / \partial z)_{\tau_i} = 0 \quad (7.2)$$

where x , y and z are spatial coordinates.

In a continuous flow stirred-tank reactor, the concentrations of the participating substances in the exit stream at time τ_i are precisely equal to the concentrations of the same substances in the reactor.

For the assumptions made above to be satisfied, one more assumption should be made: A transition from one concentration to another in an ideal stirred-tank reactor should be instantaneous. That is, a change in the concentration of a reactant from its initial concentration in the inlet stream, $C_{J,0}$, at time τ_i to the concentration in the reactor C_J must be abrupt.

The ideal condition of perfect mixing can be approximated by vigorously agitating the reaction mixture by various mechanical agitators (or stirrers) or by recirculating pumps which cause the reactor's contents to circulate around more than once during their residence time. Most easily this can be done in a tank reactor whose diameter is about equal to its height.

Let us write a mathematical model for a homogeneous, isothermal ideal stirred-tank reactor. As already noted, mathematical models for chemical reactors are based on mass and energy balances. Since we are concerned at the moment with a rigorously isothermal reactor, we may omit its heat balance and may not go into details as to how the temperature of the reaction mixture is maintained at a constant value.

Because, in accord with Eqs. (7.1) and (7.2), the concentrations of the substances that take part in the reaction in an ideal stirred-tank reactor are distributed uniformly throughout the reactor volume, the latter may be taken as the volume element to be used in the balance equations. In the general case, the process variables may change with time (that is, the reac-

tor may operate under unsteady-state conditions). Therefore, we will write the balance over an infinitesimal time interval $d\tau$.

When writing a material balance on substance J which is one of the participants in the reaction, we will deem the following:

- the volumetric flow rate of reaction mixture at the reactor inlet is v_0 (m^3hr^{-1}), and that at the outlet, v ;
- the concentration of substance J in the stream entering the reactor is $C_{J,0}$ (kmol m^{-3});
- the concentration of the same substance in the exit stream and at any point inside the reactor over a given time interval is C_J (kmol m^{-3});
- the rate of reaction is w_{rJ} ($\text{kmol m}^{-3} \text{h}^{-1}$) as measured over the specified time interval $d\tau$ at a constant temperature and determined by the concentration C_J .

Then, over the time $d\tau$:

- the quantity of J entering the reactor will be

$$n_{J,in} = C_{J,0}v_0d\tau$$

- the quantity of J used up in the reaction will be

$$n_{J,r} = w_{rJ}Vd\tau$$

- and the quantity of the substance leaving the reactor will be

$$n_{J,out} = C_Jvd\tau$$

Since the reactor holds a total of C_JV of substance J at any instant, the change in this quantity at the end of the time interval $d\tau$ will be

$$n_{J,acc} = d(C_JV)$$

Hence, the material balance on J over a perfectly mixed reactor will take the form *

$$C_{J,0}v_0d\tau - C_Jvd\tau - w_{rJ}Vd\tau = d(C_JV) \quad (7.3)$$

All terms in Eq. (7.3) are expressed in kilomoles. On dividing the left- and right-hand sides of Eq. (7.3) by $d\tau$, we get

$$C_{J,0}v_0 - C_Jv - w_{rJ}V = d(C_JV)/d\tau \quad (7.4)$$

where the terms are the molar flow rates of substance J .

The right-hand side of Eq. (7.4), which is the derivative of the quantity of J with respect to time, is the rate at which it is accumulated in the reactor.

* In Eq. (7.3), the quantity of J used up in the reaction takes a ‘-’ sign — this is correct if J is a reactant. If it is a product, w_{rJ} should be replaced with a rate equation in which the signs are chosen in accord with a formal rule (see Sec. 3.2). Thus, for the reaction $A \rightarrow R$, the rate with respect to R is

$$w_{rR} = -dC_R/d\tau = -kC_A$$

Since the reactor volume V is constant, the rate of accumulation may be written as $VdC_J/d\tau$. If the process in the reactor proceeds under steady-state conditions, the concentration of J remains unvarying with time, and so

$$dC_J/d\tau = 0$$

Under unsteady-state conditions, the right-hand side of the material balance is non-zero.

Material-balance equation (7.4) is common to any ideal stirred-tank reactors. Let us see how it works when applied to two cases, one involving an ideal batch stirred-tank reactor which always operates under unsteady-state conditions, and the other involving an ideal continuous flow stirred-tank reactor which operates under steady-state conditions.

The ideal (batch) stirred-tank reactor. In this type of reactor, all reactants are admitted prior to the onset of a chemical reaction and all products are withdrawn after the process has reached completion; while the process is under way, no reactants are admitted and no products are withdrawn to and from the reactor — the total mass of the reaction mixture in the reactor remains the same, but its composition does change. When building a mathematical model, it is assumed that the reaction mixture is the same throughout the reactor volume and that its composition solely depends on its residence time in the reactor.

The material balance over an ideal batch stirred-tank reactor is a special case of Eq. (7.4), subject to the condition that $v_0 = 0$ and $v = 0$:

$$-w_{rJ}V = d(C_J V)/d\tau \quad (7.5)$$

or

$$-w_{rJ} = dC_J/d\tau \quad (7.6)$$

Equation (7.6) is the same as Eq. (3.2) which defines the rate of a chemical transformation. Since the two equations are the same in form, we may infer that the flow pattern in an ideal batch stirred-tank reactor does not impose any constraints on the chemical kinetics of the process.

To make computations on the basis of Eq. (7.6), the applicable rate equation $w_{rJ}(C_J)$ should be used instead of w_{rJ} on its left-hand side. Then we will be able to compute, say, the reaction time required in order to achieve the desired degree of conversion:

$$\tau = - \int_{C_{J,0}}^{C_J} [dC_J/w_{rJ}(C_J)] \quad (7.7)$$

If J is a reactant, its concentration, C_J , may be expressed in terms of its fractional conversion:

$$C_J = C_{J,0}(1 - x_J) \quad (7.8)$$

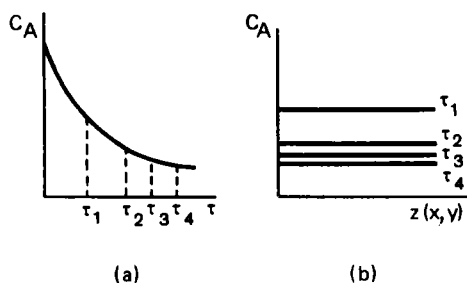


Fig. 7.2 Variations in reactant concentration in a perfectly mixed batch-type reactor: (a) with time and (b) over reactor volume

Then,

$$dC_J = -C_{J,0} dx_J \quad (7.9)$$

and Eq. (7.7) takes the form

$$\tau = C_{J,0} \int_0^{x_J} [dx_J / w_{rJ}(x_J)] \quad (7.10)$$

Using Eqs. (7.7) and (7.10), we can also compute C_J or x_J as a function of the residence time (the reaction time). The conditions in a batch reactor (the concentrations of the reactants and products, the reaction rate, etc.) change from one instant of time to the next. At any given instant, however, they are precisely the same throughout the reactor volume under the assumption of perfect mixing in the reactor (Fig. 7.2).

The time computed by Eq. (7.7) or Eq. (7.10) is the “net” time required for a chemical change to take place. When a process is carried out in a batch reactor, however, some more time has additionally to be spent in order to load a fresh batch of reactants, to bring up the reactor to the desired operating level, to discharge the products, and to clean the reactor. The total time of one operating cycle of a batch reactor is the sum of the reaction time, τ_r , and the auxiliary (or handling) time, τ_{aux} :

$$\tau_\Sigma = \tau_r + \tau_{aux} \quad (7.11)$$

Because of the auxiliary time, the throughput of the reactor (that is, the quantity of product obtained per unit time) is reduced, and this is a major limitation of batch processes in general. Other drawbacks are reliance on manual labour and the fact that such processes are not readily adaptable to automatic control (because the conditions in the reactor are changing all the time).

On the other hand, batch reactors are readily adaptable to a wide range of reaction conditions, which is an obvious convenience when one and the same reactor has to be used to make a wide range of products. For this reason commercial batch stirred-tank reactors which come very closely to

the ideal batch stirred-tank reactor, are widely used in the manufacture of reagents, organic dyes, and drugs, that is, in applications where a sufficient degree of conversion may be achieved over a relatively long time, but the scale of production is small.

Batch stirred-tank reactors are often employed in the microbiological industry to cultivate aerobic microorganisms. For most microorganisms the cultivation time is 48-72 hours which is a rather long span of time. Vigorous agitation in a fermenter assures a uniform temperature distribution which is especially important in processes where even a negligible local heat build-up might kill the microorganisms. Since the reaction system is isolated in a batch reactor, it is an easy matter to avoid any risk of poisoning the microorganisms such as may happen by inadvertently permitting some objectionable impurities to find their way into a continuous flow reactor.

The final decision on whether to use a batch or a continuous process can be made only after a thorough economic evaluation (by comparing the costs of operation, wear and tear, utilities, etc.). As a rule, such an evaluation will usually show that batch processes are advantageous where a small-capacity plant is used to manufacture expensive products.

The ideal continuous flow stirred-tank reactor under steady-state conditions. When a product is to be turned out in large quantities and of a consistent quality, preference is given to continuous reactors operating under steady-state conditions. One form is the continuous flow stirred-tank reactor. It may operate under unsteady-state conditions (at start-up, when coming up to its rated operating conditions, and at shut-down) and under steady-state conditions.

Consider the material balance over an ideal continuous flow stirred-tank reactor operating under steady-state conditions and without a recycle. It can readily be deduced from the general material balance, Eq. (7.4), over an ideal stirred-tank reactor assuming that the rate of accumulation is zero:

$$C_{J,0}v_0 - C_Jv - w_{rJ}V = 0 \quad (7.12)$$

The process in a continuous flow reactor will proceed under steady-state conditions when the volumetric flow rate is the same at the inlet to and the exit from the reactor, v_0 and v , respectively. Then,

$$v(C_{J,0} - C_J) - w_{rJ}V = 0 \quad (7.13)$$

Equation (7.13) may be re-cast as

$$V/v = \bar{\tau} = (C_{J,0} - C_J)/w_{rJ} \quad (7.14)$$

The quantity

$$\bar{\tau} = V/v$$

in Eq. (7.14) has the units of time and represents the mean time during which the contents of a continuous reactor are renewed. Technically, it is called the *mean residence time* of the reactants in a continuous flow reactor.

The actual residence time of reacting species in a continuous flow stirred-tank reactor is a random quantity in contrast to the residence time of reactants in a batch reactor. Let, as an example, N identical species be admitted to a reactor. In a batch reactor they will all reside during the same time from charging to discharge. In an ideal continuous flow stirred-tank reactor these species are distributed throughout the reactor volume uniformly and instantaneously. Since, however, the stream of products is leaving the reactor all the time, some quantity of reactants may find itself in the exit stream the same instant as they enter the reactor. On the other hand, some species, uniformly distributed in fresh portions of the reaction mixture entering the reactor may stay in it for an infinitely long time. Therefore it may be concluded that the actual residence time of particles in a continuous flow reactor is a random variable which may range in value from zero to infinity. A continuous random variable can be specified by giving its probabilistic characteristics, notably its distribution function.* It is convenient to use $\bar{\tau}$ as the residence time of a particle in a continuous stirred-tank reactor because it is directly related to the volume of the reactor and the volumetric flow rate of the reaction mixture.

For practical applications it is convenient to express the reactant concentration C_J in terms of the fractional conversion x_J . Then,

$$\bar{\tau} = V/v = C_{J,0}x_J/w_{r,J} \quad (7.15)$$

The material balances, Eqs. (7.14) and (7.15), over an ideal continuous stirred-tank reactor under steady-state conditions differ in several respects from those over a batch reactor, Eqs. (7.7) and (7.10). For one thing, the balances over an ideal continuous stirred-tank reactor under steady-state conditions can be written directly in the form of a finite-difference algebraic equation while those over a batch reactor take the form of differential equations.

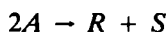
In the balance over a batch reactor, the reaction rate $w_{r,J}$ should be written as a function of concentration, $w_{r,J}(C_J)$, or as a function of fractional conversion, $w_{r,J}(x_J)$, and the respective numerical values can be substituted only after the equation has been integrated. This fact, along with the differential form of the material balance, reflects the time dependence of the process variables in a batch reactor. Under steady-state conditions, the concentration remains constant at any point in ideal stirred-tank reactor at any instant of time. In consequence, the reaction rate for such a reactor

* In more detail this matter is discussed in Chap. 8.

takes an only value determined by the concentration. This value may directly be substituted in the material balance.

Example 7.1 Compute the mean residence time required for reactant A in a continuous stirred-tank reactor to achieve a fractional conversion of $x_A = 0.8$.

The reaction taking place in the reactor is a 2-nd order reaction



whose constant-temperature rate is described by the rate equation

$$w_{rA} = 2.5C_A^2$$

The initial concentration of reactant A at the inlet to the reactor is

$$C_{A,0} = 4 \text{ kmol m}^{-3}$$

Solution. The value of $\bar{\tau}$ can be found by Eq. (7.15). The reactant concentration required for the computation of the reaction rate can be expressed in terms of the respective fractional conversion

$$\begin{aligned}\bar{\tau} &= C_{A,0}x_A/w_{rA} = C_{A,0}x_A/kC_A^2 = C_{A,0}x_A/kC_{A,0}^2(1 - x_A)^2 \\ &= 0.8 \div 2.5 \times 4(1 - 0.8)^2 = 2 \text{ hr}\end{aligned}$$

Thus, for x_A to be 0.8, the ratio of reactor volume to volumetric flow rate through the reactor should be

$$\bar{\tau} = V/v = 2 \text{ hr}$$

The material balance over a continuous flow reactor may be used not only to find the mean residence time and, hence, the size of the reaction space, $V = v\bar{\tau}$, for a given degree of conversion, but also to solve the inverse problem: Given the reactor volume and the throughput in terms of the reactant (which is proportional to the volumetric flow rate v), to find the exit concentration of the products. It is an easy matter to solve this problem if the reaction rate is described by a relatively simple rate equation (1st or 2nd-order). As an example for the 1st-order reaction



it follows from the material balance, Eq. (7.14), that

$$\bar{\tau} = (C_{A,0} - C_A)/kC_A$$

and

$$C_A = C_{A,0}/(1 + k\bar{\tau}) \quad (7.16)$$

As often as not, the rate of complex reactions proceeding by an incompletely known mechanism is expressed by an equation of a fractional

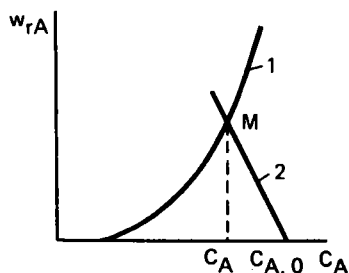


Fig. 7.3 Graphical determination of reactant concentration at the exit from a continuous perfectly mixed reactor

order. In such cases, an analytical solution is out of the question, and one has to resort to numerical methods of computation. One example is a graphical method of determining the exit concentration of the substances leaving a well-stirred continuous reactor.

The material balance defined by Eq. (7.14) may be re-cast as

$$w_{rA} = C_{A,0}/\bar{\tau} - C_A/\bar{\tau} \quad (7.17)$$

Equation (7.17) is an equality involving two different functions of concentration. Its left-hand side is the function $w_{rA}(C_A)$ which is a rate equation. In accord with the mass action law, the reaction rate is proportional to the reactant concentrations. Therefore, $w_{rA}(C_A)$ is an increasing function which can readily be presented in graphical form (curve 1 in Fig. 7.3). It cuts the axis of abscissas at a point corresponding to the equilibrium concentration $C_{A,e}$ for reversible reactions or starts at the origin for irreversible reactions.

The right-hand side of Eq. (7.17) is a linear functional relation connecting the rate reaction to the concentration of the reactant. It has a negative slope $(-1/\bar{\tau})$ and its plot is the straight line cutting the axis of abscissas (the concentration axis) at the point $C_A = C_{A,0}$ (curve 2 in Fig. 7.3).

Equation (7.17) is satisfied by the values of C_A such that the functions on the left- and right-hand sides are equal, that is, by the concentrations at which the respective curves intersect. As is seen from Fig. 7.3, curves 1 and 2 intersect at only one point, M . The abscissa of this point is the sought exit concentration of the substance leaving a continuous flow stirred-tank reactor.

7.2 The Ideal (Plug Flow) Tubular Reactor

An ideal tubular reactor is a long conduit through which the reaction mixture progresses as a plug (Fig. 7.4). This is the reason why it is referred to also as a plug flow tubular reactor. Each plug may be visualized as a fluid element separated by two planes passing at right angles to the axis of the conduit and moving down the conduit so that it displaces all the plugs

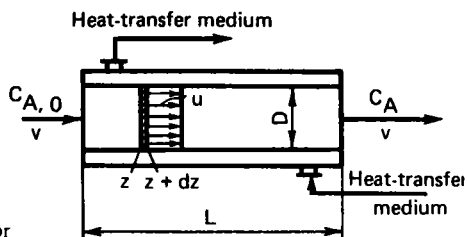


Fig. 7.4 Sketch of a plug flow reactor

located ahead and does not mix with the material either ahead or behind. In contrast to perfect or complete mixing, this condition can only exist in continuous flow tubular reactors.

The ideal condition known as plug flow can exist only if the following requirements are satisfied.

- (1) The moving stream has a flat linear velocity profile.
- (2) There is complete mixing laterally and little or no longitudinal mixing (axial dispersion or backmixing) between the plugs at different positions along the reactor, whatever the cause of mixing may be.

It is important to note that these two requirements are not met by real reactors. As fluid dynamics tells us, even in a very smooth conduit the flow of fluid is characterized by high values of the Reynolds number, and there is a viscous boundary layer at the walls where the radial linear velocity gradient is very high. Figure 7.5 shows velocity profiles for a laminar flow, a highly turbulent flow, and an ideal plug flow. As is seen, the best approximation to the ideal plug flow is only possible when the flow is highly turbulent.

Unfortunately, a turbulent flow is characterized by irregular pulsations occurring in a chaotic manner. Because of them, some fluid elements may move ahead of, or lag behind, the main stream. The result will be a partial longitudinal mixing. Of course, the associated displacements of the fluid elements will be negligible in comparison with the displacement of the main body of the stream. In a real reactor, it is possible to come very closely to the ideal plug flow if the reaction mixture flows as a turbulent stream and

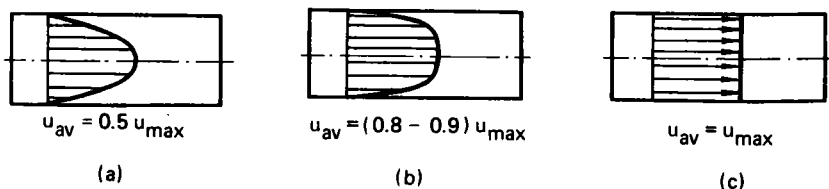


Fig. 7.5 Linear velocity profiles for (a) a laminar flow, (b) a highly turbulent flow and (c) a plug flow

the length of the conduit is many times its cross-sectional dimensions (for tubular reactors, $L/D > 20$).

Let us write a material balance over an ideal plug-flow reactor. Since there is no longitudinal mixing as a reaction takes place in the reactor, the concentrations of the participating substances will be distributed other than uniformly along the reactor. Therefore, the element of volume over which balances are written must be infinitesimal. Let us suppose that in a conduit of a constant cross-sectional area A two parallel planes spaced a distance dz apart select an element of volume $dV = A dz$ (see Fig. 7.4). Owing to strong turbulent pulsations, there is a uniform radial distribution of concentrations within the volume element dV . In the general case, ideal plug flow reactors operate under unsteady-state conditions; in consequence, the element of time over which the balance is written will likewise be infinitesimal, $d\tau$.

In view of the foregoing it is obvious that the concentration of substance J on which the balance is written is a function of two variables — the coordinate (distance) z and the time τ :

$$C_J = C_J(z, \tau)$$

As the z -coordinate changes (on leaving the volume element), the change in the concentration C_J is $(\partial C_J / \partial z) dz$, while a change in time by $d\tau$ causes the concentration to increment by $(\partial C_J / \partial \tau) d\tau$.

The material balance on substance J over an element of volume selected in an ideal plug flow reactor at a constant volumetric flow rate v , written similarly to Eq. (7.3), takes the form

$$v C_J d\tau - v \left(C_J + \frac{\partial C_J}{\partial z} dz \right) d\tau - w_{r,J} dV d\tau = \left(\frac{\partial C_J}{\partial \tau} d\tau \right) dV \quad (7.18)$$

On dividing the above equation termwise by $dV d\tau = A dz d\tau$, we get

$$-(v/A)(\partial C_J / \partial z) - w_{r,J} = \partial C_J / \partial \tau \quad (7.19)$$

Because $v/A = u_z$ is the linear velocity of the stream along the axis of the reactor, Eq. (7.19) may be re-cast as

$$-u_z(\partial C_J / \partial z) - w_{r,J} = \partial C_J / \partial \tau \quad (7.20)$$

As fluid dynamics tells us, the first term in Eq. (7.20) describes the change in the concentration of substance J due to convective transport, that is, the change in its concentration due to changes in the z coordinate as a result of an ordered displacement of the reaction stream. The second term of Eq. (7.20) describes the change in the concentration of substance J as a result of a chemical reaction. If the two changes are not the same in magnitude, substance J will be accumulated in the volume element, and the right-hand side of Eq. (7.20) will be other than zero.

Now let us discuss an ideal plug flow reactor under steady-state conditions.

Under steady-state conditions, the volumetric flow rate v through the reactor remains unchanged. Then, on recalling that $Az/v = V/v = \bar{\tau}$, we may write Eq. (7.20) as

$$-dC_J/d\bar{\tau} - w_{rJ} = 0 \quad (7.21)$$

It is to be stressed once more than the mean residence time of the reactants in a continuous flow reactor, $\bar{\tau}$ (which characterizes in the case of a plug flow reactor the time it takes for the stream to travel the distance from the inlet to some point z on its axis) is physically different from the quantity τ on the right-hand side of Eq. (7.20) — the time during which the process variables undergo a change at some fixed point inside the reactor.

Equation (7.21) which applies to an ideal plug flow reactor under steady-state conditions may be integrated with respect to $\bar{\tau}$:

$$\bar{\tau} = - \int_{C_{J,0}}^{C_J} \frac{dC_J}{w_{rJ}(C_J)} \quad (7.22)$$

or, if J is the reactant,

$$\bar{\tau} = C_{J,0} \int_0^{x_J} \frac{dx_J}{w_{rJ}(x_J)} \quad (7.23)$$

Equations (7.22) and (7.23) look like Eqs. (7.7) and (7.10) for an ideal batch stirred-tank reactor.

If we assume that the element of volume dV over which the material balance is written can move along with the stream, it may be treated under the plug flow conditions as a kind of microscopic ideal batch stirred-tank reactor the reaction time in which is equal to the mean residence time of the materials in an ideal plug flow reactor.

Equations (7.22) and (7.23) may be used to compute the size of an isothermal ideal plug flow reactor and the degree of conversion it assures.

Example 7.2 Find the mean residence time in the ideal plug flow reactor of Example 7.1, that is, for the 2nd-order reaction $2A \rightarrow R + S$, the rate equation $w_{rA} = 2.5C_A^2$, $C_{A,0} = 4 \text{ kmol m}^{-3}$, and $x_A = 0.8$.

Solution. Using Eq. (7.23), we get

$$\bar{\tau} = V/v = C_{A,0} \int_0^{x_A} [dx_A / kC_{A,0}^2(1 - x_A)^2]$$

$$\begin{aligned}
 &= (1/kC_{A,0})[x_A/(1 - x_A)] \\
 &= [1 \div (2.5 \times 4)][0.8 \div (1 - 0.8)] = 0.4 \text{ hr}
 \end{aligned}$$

Thus, if we wish to obtain the same results, the mean residence time $\bar{\tau}$ for a plug flow reactor should be substantially shorter (0.4 hr) than for a continuous flow stirred-tank reactor.

7.3 Comparison of Ideal Continuous Flow Stirred-Tank and Plug Flow Tubular Reactors in Terms of Efficiency

As is seen from Examples 7.1 and 7.2, given the same reaction conditions, the same reaction, and the same degree of conversion, the mean residence time is greater for the ideal continuous flow stirred-tank reactor than it is for the plug flow reactor. This difference can readily be traced back to the distribution of the reactant and product concentrations throughout the reaction volume in each case. While in an ideal continuous flow stirred-tank reactor the concentration at any point is equal to the final concentration (curve 1 in Fig. 7.6), in a plug flow reactor the reactant and product concentrations at one point on the reactor axis differ from those at another (curve 2 in Fig. 7.6). For example, as follows from Eq. (7.22) for a 1st-order reaction, $w_{rA} = kC_A$, the concentration distribution for reactant A is described by the equation

$$C_A = C_{A,0} \exp(-kz/u_z)$$

By the mass action law, the reaction rate is proportional to the concentration of the reactants. In consequence, in a plug flow tubular reactor it is always higher than in a continuous flow stirred-tank reactor. Since, however, the reaction rate is higher, a shorter time is needed in order to achieve the same degree of conversion.

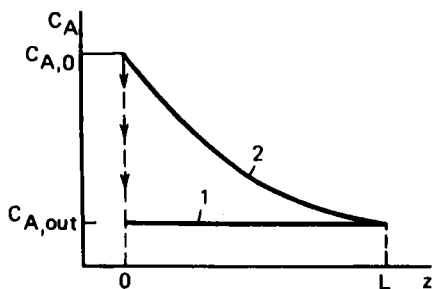


Fig. 7.6 Reactant concentration distribution along reactor axis in (1) a perfectly mixed continuous reactor and (2) a plug flow continuous reactor

In an easy-to-grasp form these relations can be established from a graphical comparison of the mean residence time for both types of continuous flow reactors.

Let us compare the two types of reactors in terms of efficiency in the case of simple reactions not complicated by any side transformations. The same degree of conversion is to be achieved, and the reactor that needs a shorter mean residence time in order to achieve the specified results will be taken as the more efficient of the two.

Given a particular degree of conversion (the concentration of reactant A in the exit stream, $C_{A,out}$, or the corresponding fractional conversion $x_{A,out}$), the mean residence time for a stirred-tank reactor in accord with Eqs. (7.14) and (7.15) may be defined as the product of two constant quantities

$$\bar{\tau}_{s.t.} = (C_{A,0} - C_{A,out}) \left[\frac{1}{w_{rA}(C_{A,out})} \right]$$

or

$$\bar{\tau}_{s.t.} = x_{A,out} \left[\frac{C_{A,0}}{w_{rA}(x_{A,out})} \right]$$

where the subscript 's.t.' stands for 'stirred-tank'. Graphically, it may be drawn as a rectangle whose sides correspond each to one of the terms in the product.

For a plug flow reactor under steady-state conditions

$$\bar{\tau}_{p.f.} = - \int_{C_{A,0}}^{C_{A,out}} \frac{1}{w_{rA}(C_A)} dC_A$$

or

$$\bar{\tau}_{p.f.} = C_{A,0} \int_0^{x_{A,out}} \frac{1}{w_{rA}(x_A)} dx_A$$

where the subscript 'p.f.' stands for 'plug flow'. Graphically, $\bar{\tau}_{p.f.}$ is represented by the area of a curvilinear trapezoid bounded by the straight lines $C_A = C_{A,out}$ and $C_A = C_{A,0}$, the plot of $1/w_{rA} = f(C_A)$, and the axis of abscissas (Fig. 7.7a) or, by Eq. (7.15), by the area of a curvilinear trapezoid bounded by the straight lines $x_A = 0$ and $x_A = x_{A,out}$, the plot of $1/w_{rA} = f(x_A)$, and the axis of abscissas (Fig. 7.7b).

It is seen from Fig. 7.7 that the areas of the curvilinear trapezoids representing $\bar{\tau}_{p.f.}$ are smaller in magnitude than those of the rectangles representing $\bar{\tau}_{s.t.}$, the difference being the greater, the higher the conversion achieved. In consequence, given the same volumetric flow rate, a plug flow

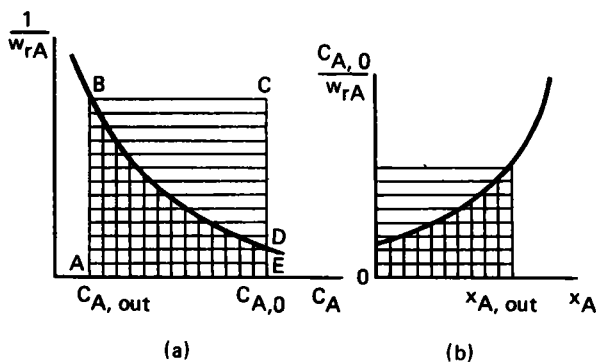


Fig. 7.7 Graphical comparison of continuous perfectly mixed and plug flow reactors as areas of geometrical shapes plotted as (a) $1/w_{rA}$ -vs- C_A or (b) $C_{A,0}/w_{rA}$ -vs- x_A

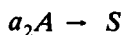
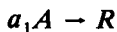
reactor needs a smaller volume than a stirred-tank reactor in order to achieve the same conversion. The specific throughput, or intensity, defined as

$$I = T/V = vC_{A,0}x_A/V$$

of a plug flow reactor will be higher. This may be traced back to the higher reaction rate in a tubular reactor owing to the higher reactant concentration.

However, it is not always desirable to maintain the reactant concentrations at high values. For example, it has been shown in Chap. 3 that in cases involving parallel reactions of different orders such that the desired reaction has a lower order than the side reaction ($n_1 < n_2$), the higher differential selectivity is obtained at lower reactant concentrations (see, for example, Fig. 3.1).

Now we will compare the two types of reactor when the reactions involved are parallel and have different orders



with respect to the yield of the desired product, R . Assume that each reactor gives the same conversion of reactant A (that is, we assume in advance that $\bar{\tau}_{p,f.} < \bar{\tau}_{s,t.}$).

By definition, the yield from irreversible parallel reactions is, in accord with Eq. (1.31), equal to

$$\Phi_R = \varphi x_A$$

In turn, the total or integral selectivity of the process, Eq. (1.27), is

$$\varphi = (C_R/\psi_{AR})/(C_{A,0} - C_A) = (C_R/\psi_{AR})/C_{A,0}x_A$$

From the definition of differential selectivity, Eq. (3.11),

$$\varphi' = -(dC_R/\psi_{AR})/dC_A \quad (7.24)$$

it follows that

$$C_R = -\psi_{AR} \int_{C_{A,0}}^{C_{A,out}} \varphi' dC_A \quad (7.25)$$

On substituting for C_R from Eq. (7.25) into Eq. (1.24), we get

$$\Phi_R = -(1/C_{A,0}) \int_{C_{A,0}}^{C_{A,out}} \varphi' dC_A \quad (7.26)$$

The differential selectivity φ' under the integration sign is in the general case a decreasing or an increasing function of the concentration of reactant A . Therefore, if C_A changes from one point in the reactor to another, this function must be integrated before the yield Φ_R can be found. Notably, this is the case when the yield of product R from a plug flow reactor is to be found. If, on the other hand, C_A is the same throughout the reactor volume and remains so with time (this happens in an ideal stirred-tank reactor operating under steady-state conditions), the differential selectivity φ' for an ideal stirred-tank reactor will likewise have a constant value and Eq. (7.26) may then be simplified as

$$\Phi_{R,s.t.} = \frac{C_{A,0} - C_{A,out}}{C_{A,0}} \varphi'(C_{A,out}) \quad (7.27)$$

The product yield, Φ_R , as found by Eq. (7.26) for a plug flow reactor and by Eq. (7.27) for an ideal stirred-tank reactor, may be represented graphically as the areas of a curvilinear trapezoid, $\Phi_{R,p.f.}$ and of a rectangle, $\Phi_{R,s.t.}$. The relative magnitude of these areas depends on the function $\varphi'(C_A)$.

If the main reaction is higher in order than the side parallel reaction ($n_1 > n_2$), the product yield Φ_R will be greater from a plug flow reactor (Fig. 7.8a). By the same token, as already noted, the mean residence time required to achieve the specified conversion will be shorter than in the case of an ideal stirred-tank reactor.

If, on the other hand, the order of the main reaction is lower than that of the side reaction ($n_1 < n_2$), a greater product yield can be obtained from an ideal stirred-tank reactor (Fig. 7.8b). In the case in question, however, that is, when the degree of conversion of the reactant is the same, the mean residence time for an ideal stirred-tank reactor, $\bar{\tau}_{s.t.}$, is longer than it is for a plug flow reactor.

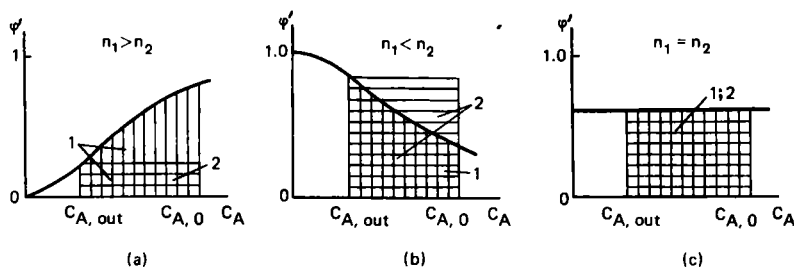


Fig. 7.8 Graphical comparison of product yield from (1) a continuous plug flow reactor and (2) a continuous perfectly mixed reactor with parallel reactions differing in order:

a, $n_1 > n_2$; *b*, $n_1 < n_2$; *c*, $n_1 = n_2$

If both the main and the side reactions are of the same order ($n_1 = n_2$), the product yield at the same level of conversion will be independent of the reactor type (Fig. 7.8c).

It follows from the above comparison that in some cases a higher yield can be obtained from a plug flow reactor while in other cases this can be done using an ideal stirred-tank reactor. It is to be stressed that even with a high product yield and the same degree of conversion an ideal stirred-tank reactor will have a larger volume than a plug flow reactor.

In the above comparison we have neglected a number of factors limiting the use of reactors operating under conditions close to the ideal plug flow. Among them are, for example, the high pressure drop across tubular reactors, the difficulty in cleaning them, etc. Physically, continuous stirred-tank reactors are simpler, but they suffer from a major disadvantage in that the concentration of the reactant settles at a low value (equal to the final concentration) so that the reaction rate is low, too. One way to fully utilize the advantages offered by stirred-tank reactors and to maintain, at the same time, higher reactant concentrations is to connect several ideal stirred-tank reactors in series, or cascade as this arrangement is commonly referred to.

7.4 The Multiple Well-Stirred Tank Cascade

As already defined, the cascade arrangement is a number of continuous well-stirred tank reactors (stages or units) connected in series (Fig. 7.9). The reaction mixture passes through the individual stages in turn. Fig. 7.10 compares the manner in which the initial reactant concentration changes as the reactant mixture passes through the individual ideal stirred-tank reactors of a cascade, a single plug flow tubular reactor, and a single continuous well-stirred tank reactor.

For a cascade of stirred-tank reactors to qualify as an ideal, the following must be satisfied.

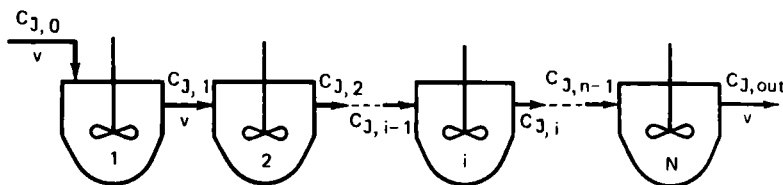


Fig. 7.9 Cascade of continuous perfectly mixed tank reactors

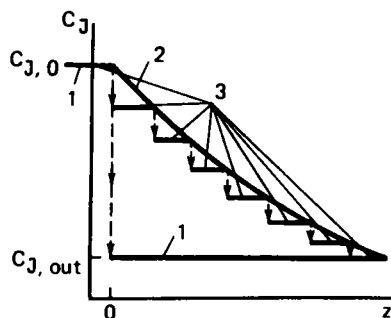


Fig. 7.10 Variations of reactant concentration in a single reactor: (1) the perfectly mixed type, (2) the plug flow type, and (3) a cascade of perfectly mixed reactors

(1) Each stage of the cascade meet the requirements for a single well-stirred or ideal stirred tank reactor — the process variables change instantaneously upon entry of the feed and become the same at any point within each stage and in the stream leaving it.

(2) Every next unit does not affect the performance of the previous one.

The mathematical model of a multiple well-stirred tank cascade operating isothermally is a set of material balances on some participant in the reaction, with at least N balance equations for as many stages in the cascade.*

The material balance over any stage in a cascade is the same in appearance as that over any other stage in the same cascade.

The material balance on component J over the i th unit of a cascade operating under steady-state conditions has the form

$$vC_{J,i-1} - vC_{J,i} - w_{rJ}(C_{J,i})V_i = 0 \quad (7.28)$$

or

$$\bar{\tau}_i = V_i/v = (C_{J,i-1} - C_{J,i})/[w_{rJ}(C_{J,i})] \quad (7.29)$$

where:

V_i = reaction volume of the i th unit in the cascade

$\bar{\tau}_i$ = mean residence (holding or space) time in the i th unit

* When modelling a cascade with a complex reaction where a material balance on any one participant would not be enough, the model will consist of a number of equations which is a multiple of N .

$C_{J,i-1}$ = concentration of component J at the inlet to the i th unit,
equal to the outlet concentration from the $(i - 1)$ st unit

$C_{J,i}$ = concentration of component J at the outlet from the i th unit

The design of a multiple well-stirred tank cascade usually reduces to finding the number of units of a specified volume, required to obtain the specified degree of conversion or to determining the composition of the reaction mixture at the outlet from the i th unit of the cascade.

The assumption that every next unit in a multiple well-stirred tank cascade does not affect the performance of the previous one substantially simplifies the design procedure. Actually, it consists in consecutively solving the equations of the mathematical model for each unit with respect to the outlet reactant (or product) concentration. The outlet variables for the first unit, $C_{J,1}$, are used as the inlet variables for the second unit, the outlet variables of the second unit as the inlet variables for the third, etc.

A multiple stirred-tank cascade may be computed using analytical or numerical methods. The analytical method applies when the equations of the mathematical model can be analytically solved with respect to C_J . This can be done if, for example, the reactions involved are described by rate equations of the 1st or 2nd order.

Let us find the concentration of reactant A at the outlet from a multiple stirred-tank cascade consisting of N units of the same volume ($V_1 = V_2 = \dots = V_i = \dots = V_N$), in which a 1st-order reaction is carried out whose rate is $w_{rA} = kC_A$. From the material balance over the 1st section

$$\bar{\tau}_1 = V_1/v = (C_{A,0} - C_{A,1})/kC_{A,1}$$

we find

$$C_{A,1} = C_{A,0}/(1 + k\bar{\tau}_1)$$

Now we substitute the above value of $C_{A,1}$ as the inlet concentration in the material balance over the 2nd unit:

$$\begin{aligned}\bar{\tau}_2 = V_2/v &= (C_{A,1} - C_{A,2})/kC_{A,2} \\ &= [C_{A,0}/(1 + k\bar{\tau}_1) - C_{A,2}]/kC_{A,2}\end{aligned}$$

and find $C_{A,2}$:

$$C_{A,2} = C_{A,0}/(1 + k\bar{\tau}_1)(1 + k\bar{\tau}_2)$$

Since all the units have the same volume, it follows that

$$\bar{\tau}_1 = \bar{\tau}_2 = \dots = \bar{\tau}_i = \dots = \bar{\tau}$$

and then

$$C_{A,2} = C_{A,0}/(1 + k\bar{\tau})^2$$

Proceeding in the same manner, we get for the N th (last) unit of the cascade

$$C_A = C_{A,0}/(1 + k\bar{\tau})^N \quad (7.30)$$

On recalling that $C_A/C_{A,0} = 1 - x_A$, we may re-write Eq. (7.30) as

$$1 - x_A = 1/(1 + k\bar{\tau})^N \quad (7.31)$$

and find the number of units of the specified volume, required to obtain the desired fractional conversion x_A :

$$N = \frac{\log_{10} [1/(1 - x_A)]}{\log_{10} (1 + k\bar{\tau})} = -\log_{10} (1 - x_A) / \log_{10} (1 + k\bar{\tau}) \quad (7.32)$$

Naturally, Eq. (7.32) holds only for 1st-order reactions.

In cases involving reactions that are described by rate equations permitting of no analytical solution of Eq. (7.29) for C_j (one example is fractional-order reactions), numerical methods have to be used in the design of a multiple unit cascade. Since the material balance is the same in form for all the units of a cascade, it will suffice to work out an algorithm for solving the equations of the i th unit and then to use it N times. Of course, a computer is then needed (in the simplest case, a microcomputer will do well).

It is instructive to compute a multiple unit cascade by the graphical method employed to determine the reactant concentration at the outlet from a well-stirred tank reactor. The procedure remains the same. To begin with, the equation describing the 1st unit

$$w_{rA}(C_{A,1}) = C_{A,0}/\bar{\tau}_1 - (1/\bar{\tau}_1)C_{A,1} \quad (7.33)$$

is solved and the concentration $C_{A,1}$ is found by constructing (Fig. 7.11) the rate curve $w_{rA}(C_A)$ and by drawing a straight line whose slope is $(-1/\bar{\tau}_1)$ and which cuts the axis of abscissas at point $C_{A,0}$. After $C_{A,1}$ is found, the equation describing the 2nd unit

$$w_{rA}(C_{A,2}) = C_{A,1}/\bar{\tau}_2 - (1/\bar{\tau}_2)C_{A,2} \quad (7.34)$$

is solved.

The concentration at the outlet from the N th reactor is found by repeating the above graphical solution N times.

If the objective is to determine the number N of units required to obtain the desired fractional conversion x_A , the graphical solution is carried on

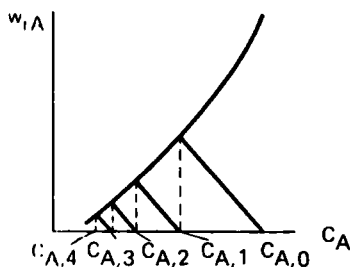


Fig. 7.11 Graphical computation of a cascade of equal-volume perfectly mixed reactors

until the abscissa of the intersection between the straight line

$$y = C_{A,i-1}/\bar{\tau}_i - (1/\bar{\tau}_i)C_{A,i}$$

and the $w_{rA}(C_A)$ curve satisfies the condition

$$C_{A,i} \leq C_{A,0}(1 - x_A) \quad (7.35)$$

Example 7.3 A multiple well-stirred tank cascade is used to effect the reaction described in Example 7.1 and 7.2. This is a 2nd-order reaction of the form



whose rate equation is

$$w_{rA} = 2.5C_A^2$$

The final fractional conversion is $x_A = 0.8$, and the initial concentration of reactant A is $C_{A,0} = 4 \text{ kmol m}^{-3}$. All the stages of the cascade have the same volume selected so that the mean residence time in each, $\bar{\tau}$, is one-tenth of the mean residence time in the single well-stirred tank reactor computed in Example 7.1 ($\bar{\tau} = 0.2 \text{ hr}$). Find how many such reactors are needed in order to obtain the desired degree of conversion.

Solution. We choose to solve the problem graphically. To this end, we plot the functions

$$w_{rA} = 2.5C_A^2$$

(a parabola) and

$$\begin{aligned} y &= C_{A,0}/\bar{\tau} - (1/\bar{\tau})C_A \\ &= 4 \div 0.2 - (1 \div 0.2)C_A \end{aligned}$$

(a straight line whose slope is

$$\tan \alpha = -1/\bar{\tau} = -5.0).$$

The intersection of the two plots, point M_1 in Fig. 7.12, makes it possible to find the concentration at the outlet from the first unit of the cascade. On drawing the parallel lines

$$y = C_{A,i-1}/\bar{\tau} - (1/\bar{\tau})C_{A,i}$$

until the condition

$$C_{A,i} \leq 0.8 \text{ kmol m}^{-3}$$

is satisfied (because

$$\begin{aligned} C_{A,out} &= C_{A,0}(1 - x_A) \\ &= 4(1 - 0.8) = 0.8 \text{ kmol m}^{-3} \end{aligned}$$

we find that in order to obtain this degree of conversion, we need 4 units. With this choice of the cascade arrangement, we also find that the degree

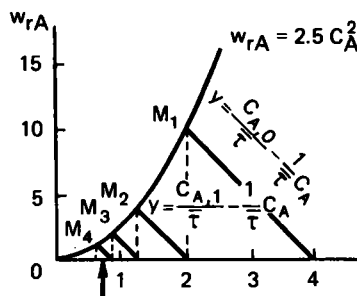


Fig. 7.12 To Example 7.3

of conversion at the outlet from the 4th unit will be even greater than is required by the statement of the problem, but this figure would not have been achieved with three units.

Thus, the overall mean residence time for the multiple well-stirred tank cascade of Example 7.3 is

$$\bar{\tau}_{\Sigma, \text{casc}} = 4\bar{\tau} = 0.8 \text{ hr}$$

which is greater than the figure found for a single ideal plug flow reactor ($\tau_{p.f.} = 0.4 \text{ hr}$; see Example 7.2), but is shorter than for a single ideal stirred-tank reactor ($\bar{\tau}_{s.t.} = 2 \text{ hr}$; see Example 7.1).

Chapter Eight

CHEMICAL REACTORS WITH NON-IDEAL FLOW PATTERNS

In developing mathematical models for the continuous well-stirred tank reactor and the continuous plug-flow tubular reactor, we made a number of simplifying assumptions. This was done to ease both the model-building and the associated computations. A real reactor, however, often falls short of the ideal. In the sections that follow we will discuss why this deviation from the ideal happens and then build mathematical models for real reactors.

8.1 Causes of Deviation from Ideal Flow Patterns in Real Continuous Flow Reactors

In a nutshell, the operation of a continuous flow reactor may be described thus: The reactants are pumped at a constant rate into the vessel

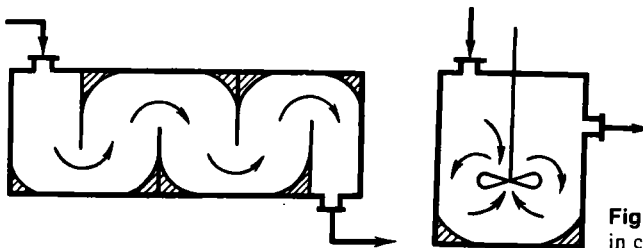


Fig. 8.1 Stagnation zones in continuous reactors

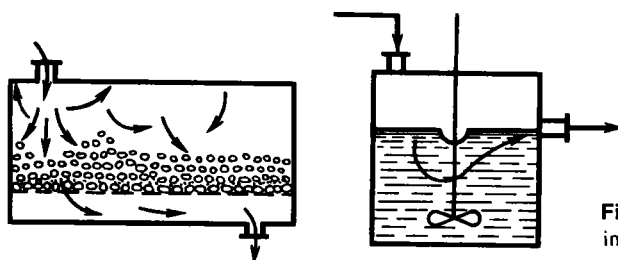


Fig. 8.2 Internal bypassing in reactors

and the reaction mixture, or the feed, is caused in one way or another to move from inlet to outlet. It is assumed that the reactants stay in the vessel for some time during which a chemical reaction can take place. In the general case, the residence time of the individual fluid elements in a continuous flow reactor is a random variable whose value may range from zero to infinity. It may so happen that some fluid element will fail to take part in the reaction because inside the reactor it finds itself in what is called a *zone of stagnation* (a *stagnant pocket*). In this zone, the flow of the reaction mixture is impeded, and the reaction rate is substantially lower than it is in the main body of the stream, if not equal to zero. A stagnant pocket may form in more than one way, as shown in Fig. 8.1.

Another cause behind the failure of some of the reaction stream to take part in the reaction is what may be called *internal bypassing* (Fig. 8.2). This condition occurs especially often in poorly engineered reactors where the reaction space is the surface of a catalyst bed.

The best result would be obtained if all the elements of the reaction stream stayed in the reaction zone during a precisely equal time. This is achievable in plug-flow tubular reactors with a flat linear velocity profile. In real reactors, however, including those that come very closely to the ideal plug flow condition, there is a distribution of fluid elements by residence time, probably because of longitudinal or axial back-mixing. This back-mixing can, for example, have its origin in *molecular diffusion*: the reactant concentration does not remain constant between two consecutive points along the tubular reactor, and the concentration gradient

Fig. 8.3 A diffused plug flow under laminar conditions (Taylor diffusion caused by a nonuniform velocity field):

1, initial position of fluid elements at an arbitrary section at time τ_1 ; 2, position of fluid elements at an arbitrary section at time τ_2 ; 3, same, at time τ_3

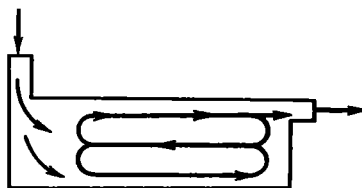
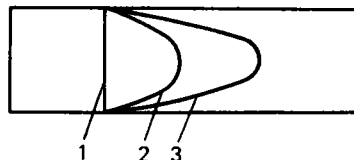


Fig. 8.4 Circulation zones in a plug flow reactor

ΔC will be the driving force for the diffusion. Longitudinal diffusion disturbs the plug flow pattern — the plug is ‘eroded’, if we treat a fluid element as a plug.

Molecular diffusion in tubular reactors is accompanied by what is called *eddy diffusion*. This form of diffusion is associated with turbulence. A turbulent stream displays chaotic pulsations of velocity relative to its mean value, these pulsations being in all directions. Those occurring radially serve to equalize the conditions (concentration, temperature) over the cross-section of the stream and are, therefore, essential in plug-flow tubular reactors. In contrast, axial pulsations result in that some fluid elements run ahead of the main body of the stream while others lag behind it, thus leading to mixing or diffusion.

Longitudinal diffusion may occur not only due to turbulence. It may also be a consequence of the fact that the velocity field is other than uniform — a thing which happens under laminar flow conditions. Now the fluid elements at the axis of the conduit have a linear velocity which exceeds that of the remaining fluid elements, $u_{av} = u_{max}/2$. If we label the fluid elements that find themselves at time τ_1 at some section, these labelled elements will show up at later times τ_2 , τ_3 , etc. at the surface of a paraboloid. The elements moving along the axis of the conduit will have moved farthest; the elements at the periphery of the stream will not have moved at all — their velocity is zero (Fig. 8.3). Although the fluid elements are not moving chaotically (we may predict the position of any selected fluid element at any instant), the result is the same as in the case of molecular diffusion — the plug is ‘eroded’. This form of diffusion caused by a nonuniform velocity field is referred to as *Taylor diffusion*.

Apart from stagnation zones, a continuous plug flow reactor may have circulation zones (Fig. 8.4) in which the reaction mixture stays much longer than the main body of the stream which flows through the reactor during a

time shorter than the mean residence time

$$\bar{\tau} = V/v = AI/v$$

because it is not distributed over all of the cross-sectional area of the reactor.

All of the above causes may result in deviations from the two extreme cases — perfect or complete mixing and the plug flow, and there would be inevitable errors in reactor calculations based on the mathematical models built on the assumption of an ideal flow pattern.

Reactor theory offers a wide choice of models which take care of the fact that the actual flow pattern in a reactor is other than ideal. These models are to a certain extent approximate too, but they are more accurate in describing real processes than the perfect mixing and plug flow models.

To begin with, we will examine models that enable the designer to visualize a process in a reactor with real flow conditions. Then we will dwell in brief on the methods used to analyse the flow pattern in chemical reactors and to decide on which of the models suits the case on hand best of all.

8.2 Models of Reactors with Non-Ideal Flow Patterns

Two approaches may be used in setting up mathematical models of non-ideal reactors. With one of them, a given reactor is mentally replaced with a combination of idealized reactors. With the other, which is more justified physically, the mathematical model of a process is built so as to take into account all the actual physical phenomena taking place in the reactor and to represent them in the model equations by means of suitable mathematical operators.

Obviously, the mathematical model based on the first approach will be a system of equations which describe between them a combination of several idealized reactors. The number of equations may be great, but they remain as simple in form as the equations describing the idealized reactors. With the second approach, fewer equations may be involved, but the equations themselves are more elaborate and would therefore require more elaborate procedures for their solution.

When developing a particular model, it is important to remember that theory usually gives the relevant equations in general form, and their coefficients, whose values differ from one particular case to another, have to be found by experiment. These numerical coefficients are referred to as the *parameters of a mathematical model*. As a rule, every effort is made to reduce their number as far as possible. In fact, it would seem that a greater number of parameters makes the model more accurate (physically). However, the risk of critical errors creeping in is in-

creased. Also, a model with a great number of parameters calls for a more accurate and exact experiment to be made so that they can be evaluated properly.

Most often, use is made of two univariate (one-parameter) models. One is the cascaded model, and the other is the dispersion model.

The cascaded model. The cascaded model uses the first approach to the description of real reactors, namely: a real reactor is mentally divided into N well-stirred stages connected in series, as shown in Fig. 8.5. The sum of the volumes of the individual stages, or cells, is equal to the total volume of the reactor.

The validity of this replacement can be borne out by comparing a multiple well-stirred tank cascade with a single well-stirred tank and a plug-flow tubular reactor.

Obviously, when $N = 1$, the cascade reduces to a single well-stirred tank reactor; when N tends to infinity and the volumes of the individual units, V_i , are infinitesimal, the cascade degenerates into a single plug flow reactor. Thus, using the multiple well-stirred tank cascade model, we can describe the two extreme cases — perfect mixing and plug flow. It is reasonable to assume that some intermediate flow patterns (such as happen in any real reactors) may likewise be described, using the model of a multiple well-stirred tank cascade consisting of N stages and recalling that N is other than unity, on the one hand, and a finite number, on the other. As a rule, a real reactor can satisfactorily be described by invoking a cascaded model with $N < 10$.

The number N of stages replacing the prototype reactor is in effect the only parameter of a cascaded model. If N is known in advance, the design of a reactor on the basis of the cascaded model will not differ from that of a multiple well-stirred tank cascade and will consist in consecutively solving the equations that model each well-stirred stage.

The one-parameter dispersion model. Similarly to the cascaded model, the dispersion model describes the actual flow pattern in a continuous flow reactor as an intermediate case between perfect mixing and the plug flow. In contrast to the well-stirred tank model, the dispersion model takes care of the variations that occur in the distribution of the process variables (notably, concentration) throughout the reactor volume. However, the concentration distribution along a plug flow tubular reactor is likewise

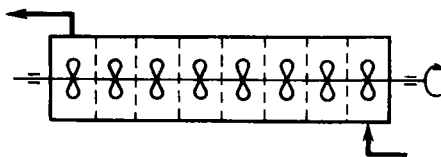


Fig. 8.5 The cascaded model

nonuniform. In contrast to the plug flow model, the dispersion model takes into account the axial mixing of the reaction mixture due to several forms of diffusion. The resultant flow is referred to as the *dispersed plug flow*. Hence the name 'dispersion model'.*

With diffusion taken into account, differential equations appear in the mathematical model because by Fick's laws mass transfer (the change in material quantity within an element of volume) by diffusion is proportional to the concentration gradient in the direction of the diffusion:

$$dn_{j,dif} = -D(dC_j/dz)$$

Therefore, the dispersion model invokes the use of a more elaborate mathematical formalism than the cascaded model does.

In a real reactor, spatial variations in the concentration distribution give rise to both axial and radial mass transfer by the diffusion mechanism. To avoid unnecessary complications in mathematical description, it is deemed to a first approximation that the radial concentration distribution is uniform and that the diffusion, or dispersion, takes place solely in the longitudinal (axial) direction.

Mass transfer by eddy or Taylor diffusion may be described by equations similar to those describing molecular diffusion but with coefficients of their own, namely D_{eddy} and D_{Tayl} . The various forms of diffusion cannot be separated from one another in a reactor. Therefore, it is reasonable to combine them in a single equation and to use a single coefficient — the *longitudinal diffusion coefficient* D_L ** which cannot be predicted in advance by theory owing to the very complex character of this quantity.

The longitudinal diffusion coefficient D_L is the only parameter of the one-parameter dispersion model.

Let us write a material balance over a reactor answering the one-parameter dispersion model. In doing so, we make the following assumptions.

- (1) As with the plug flow model, all flow conditions remain constant over the reactor's cross-section perpendicular to the main body of the stream; hence, temperature and concentration only vary along the reactor.
- (2) There are neither stagnation zones nor internal bypassing in the reactor.

When writing a material balance, it is convenient to treat a real reactor as a tubular one in which some degree of axial mixing (due to molecular,

* See A.R. Cooper & G.V. Jeffreys, *Chemical Kinetics and Reactor Design*. Oliver & Boyd, Edinburgh, 1971. — *Translator's note*.

** Since this coefficient is associated with the dispersed plug flow, Levenspiel and his co-workers gave it the name of "dispersion coefficient", D_L . — *Translator's note*.

eddy and other forms of diffusion) is superimposed, thus giving rise to a dispersed plug flow which deviates from the ideal one.

As with a plug flow tubular reactor, we select an element of reactor volume, $dV = A dz$, and an element of time, $d\tau$, and write a balance on species J . Under the assumptions made we deem that the concentration of substance J under unsteady-state conditions is a function of two variables, $C_J = C_J(z, \tau)$, while under steady-state conditions it is solely a function of the position along the reactor's axis, that is, $C_J(z)$. The feed enters the volume element dV over the time element $d\tau$ due to convective and diffusion transport.

The convective term is the same as it is for a plug flow tubular reactor

$$dn_{J,in,conv} = vC_J d\tau$$

where C_J is the concentration of substance J at a section which is z distant from the inlet to the reactor.

The diffusion term can be expressed by invoking Fick's first law. We combine all forms of diffusion and introduce the longitudinal diffusion coefficient D_L

$$dn_{J,in,dif} = -D_L A (\partial C_J / \partial z)_z d\tau$$

where $(\partial C_J / \partial z)_z$ is the concentration gradient in the direction of diffusion at a section which is z distant from the inlet to the reactor.

The quantity of reactant used up in the volume element dV is the sum of the convective and diffusion fluxes at a section which is $(z + dz)$ distant from the inlet and the quantity used up in the reaction over the time $d\tau$. As the distance from the inlet (the z -coordinate) changes, the concentration is incremented by $(\partial C_J / \partial z)dz$ and the concentration gradient is incremented by $(\partial^2 C_J / \partial z^2)dz$. Accordingly,

$$dn_{J,out,conv} = v \left(C_J + \frac{\partial C_J}{\partial z} dz \right) d\tau$$

$$dn_{J,out,dif} = -D_L A [\partial C_J / \partial z + (\partial^2 C_J / \partial z^2) dz] d\tau$$

$$dn_{J,r} = w_{r,J} dV d\tau$$

Under unsteady-state conditions, the difference between the input and output terms of the material balance is due to the accumulation of substance J in the volume element dV over the time $d\tau$:

$$dn_{J,acc} = [(\partial C_J / \partial \tau) d\tau] dV$$

Thus, the material balance in its final form is

$$\begin{aligned} & [vC_J d\tau - D_L A (\partial C_J / \partial z) dz] - [v[C_J + (\partial C_J / \partial z) dz] d\tau \\ & - D_L A [\partial C_J / \partial z + (\partial^2 C_J / \partial z^2) dz] d\tau + w_{r,J} dV d\tau] \\ & = [(\partial C_J / \partial \tau) d\tau] dV \end{aligned} \quad (8.1)$$

On dividing out all terms of the equation by $dV d\tau = A dz d\tau$ and rearranging, we get

$$-u_z(\partial C_J/\partial z) + D_L(\partial^2 C_J/\partial z^2) - w_{rJ} = \partial C_J/\partial \tau \quad (8.2)$$

where

$$u_z = v/A$$

is the linear velocity of the stream along the reactor's axis.

Equation (8.2) describes an unsteady-state process in a real distributed-parameter reactor with mixing. The flow pattern in such a reactor is described by the first two terms. The first term, $u_z(\partial C_J/\partial z)$, describes the convective transport of substance J at linear velocity u_z . The chemical reaction establishes along the reactor the concentration distribution of a given substance, described at a point z distant from the inlet by the derivative $\partial C_J/\partial z$. The second term, $D_L(\partial^2 C_J/\partial z^2)$, takes care of axial mixing whose degree is determined by the longitudinal diffusion, or dispersion, coefficient D_L .

Equation (8.2) may be used to describe the two extreme types of continuous reactor: the plug flow tubular type and the well-stirred tank type. To demonstrate, if we assume that no axial mixing takes place, then

$$D_L(\partial^2 C_J/\partial z^2) = 0$$

and Eq. (8.2) takes the same form as Eq. (7.20) for a plug flow tubular reactor:

$$-u_z(\partial C_J/\partial z) - w_{rJ} = \partial C_J/\partial \tau$$

If we assume that the concentration is uniformly distributed throughout the reactor volume, then

$$\partial C_J/\partial z = 0$$

and Eq. (8.2) may be used to design a well-stirred tank reactor.

It should be noted, however, that the design of a well-stirred tank reactor by the equation

$$D_L(\partial^2 C_J/\partial z^2) - w_{rJ} = \partial C_J/\partial \tau \quad (8.3)$$

is not so straightforward because in a well-stirred tank reactor $C_J(z)$ is a discontinuous function (at the inlet to the reactor the concentration changes stepwise from $C_{J,0}$ to the exit concentration C_J).

How closely the actual flow pattern comes to one of the extreme, or ideal, cases depends on the extent of interaction between the convective and diffusion terms in the material balance, Eq. (8.2). Using techniques of similarity theory, we may derive from Eq. (8.2) a dimensionless group which gives a measure of how any one of the two physical processes — convective transport along the axis of the reactor and diffusion mixing, or

dispersion, — is effective with respect to the other:

$$(uC/z)/(D_L C/z^2) = uz/D_L$$

where:

u = linear velocity

z = linear dimension (which may conveniently be denoted as length L).

The dimensionless group thus obtained is called the *Peclet diffusion number*

$$Pe = uL/D_L \quad (8.4)$$

At high values of the Peclet number, the intensity of convective transport is substantially higher than that of diffusion mixing. This situation exists in a long conduit (at high values of L), at a high linear velocity, or at low values of D_L . When the Peclet number tends to infinity, the reactor degenerates to a plug flow tubular reactor.

At low values of the Peclet number (a short conduit, a low linear velocity or high values of D_L), axial mixing is more intensive than longitudinal convective transport. When the Peclet number tends to zero, the reactor degenerates to a well-stirred tank reactor: as a result of the infinitely fast diffusion the concentration is made the same throughout the reactor volume instantaneously.

Design procedures based on the dispersion model are far more difficult to apply than those based on the cascaded model. The equations associated with the dispersion model can be solved analytically only for a reactor operating under steady-state conditions and effecting a 1st order reaction whose rate is a function of concentration

$$w_{rA} = kC_A$$

With the dispersion model, Eq. (8.2) takes the form

$$-u_z(dC_A/dz) + D_L(d^2C_A/dz^2) - kC_A = 0 \quad (8.5)$$

It is convenient to re-cast it as a dimensionless group on introducing a new variable

$$l = z/L$$

where L is the reactor's length. Then,

$$z = lL$$

and

$$dz = L dl$$

On noting that

$$L/u = V/v = \bar{\tau}$$

and recalling Eq. (8.4), we may re-cast Eq. (8.5) as

$$(1/Pe)(d^2C_A/dl^2) - (dC_A/dl) - k\bar{\tau}C_A = 0 \quad (8.6)$$

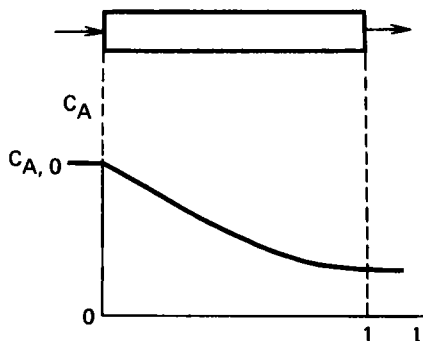


Fig. 8.6 Explaining the choice of boundary conditions to solve the differential equation of the dispersion model

Equation (8.6) is a 2nd-order differential equation. To solve it, we should specify two boundary conditions. The boundary conditions for the dispersion model were first investigated by Danckwerts, and they are often called the *Danckwerts boundary conditions*.

The choice of boundary conditions is dictated by the physical picture of the process. At $z = 0$ (that is, $l = 0$), the concentration of reactant A changes stepwise and discontinuously (Fig. 8.6) as a consequence of diffusion mixing.* Since D_L is a finite quantity, the following material balance may be written on the section $z = 0 + 0$ (that is, $l = 0 + 0$) where the chemical reaction does not yet take place:

$$vC_{A,0} - vC_A - D_L(dC_A/dz)_{z=0+0} = 0 \quad (8.7)$$

or, in terms of dimensionless coordinates,

$$(v/u)(C_{A,0} - C_A) - (1/Pe)(dC_A/dl)_{l=0+0} = 0 \quad (8.8)$$

This equation by which C_A can be computed at $z = 0$ defines the first boundary condition.

We could write a similar equation for $z = L$ (that is, $l = 1$). This would, however, result in that at the finite value of D_L and a negative derivative dC_A/dz (as z increases, C_A decreases owing to the chemical reaction that takes place), the exit stream concentration $C_{A,L}$ would be higher than the bulk concentration in the reactor. This would run contrary to physical sense, so it is reasonable in agreement with the physical nature of the process (Fig. 8.6) to adopt as the second boundary condition

$$(dC_A/dz)_{z=L-0} = 0 \quad (8.9)$$

or

$$(dC_A/dl)_{l=1-0} = 0 \quad (8.10)$$

* Compare this with the stepwise change in concentration at the inlet to a continuous well-stirred tank reactor.

For a 1st-order reaction, solving the differential equation (8.6) subject to the boundary conditions (8.8) and (8.10) yields the following result:

$$C_{A,L}/C_{A,0} = 1 - x_{A,L} = \frac{4a \exp(\text{Pe}/2)}{(1+a)^2 \exp(a\text{Pe}/2) - (1-a)^2 \exp(-a\text{Pe}/2)} \quad (8.11)$$

where

$$a = (1 + 4k\tau\text{Pe})^{1/2} \quad (8.12)$$

It is far more difficult to solve the dispersion model equations for a reaction with other kinetics. Therefore, although the dispersion model comes closest to the real physical situation, preference is often given in reactor modelling to the cascaded model as a simpler and more manageable one.*

Chapter Nine

RESIDENCE TIME DISTRIBUTION IN CONTINUOUS FLOW REACTORS

The extent to which a real flow pattern deviates from an ideal one can be determined by experiment, and the characteristics of the cascaded and dispersion models can be computed on the basis of residence time distribution analysis.

9.1 Residence Time Distribution Functions

As already noted, the residence time of fluid elements in a continuous reactor is in the general case a continuous random variable, that is, it is probabilistic in nature. A continuous random variable may be specified by giving its distribution functions. It is customary to distinguish the *integral distribution function* $F(\tau)$ and the *differential distribution function* or the *distribution density function* $f(\tau)$.

The integral residence time distribution function, $F(\tau)$, is the volumetric fraction of material in the reactor exit stream that has spent a time less than τ in the reactor **.

* It is to be noted that the computational results on the basis of the dispersion model depend, for example, on the choice of boundary conditions for the differential equation. In the case of the cascaded model, the computational procedure practically reduces to solving a system of algebraic equations.

** Its alternative name is the *internal age distribution function* which is given the symbol $I(t)$ by some authors. — *Translator's note.*

In terms of probability theory, $F(\tau_i)$ is the probability that the residence time of the stream entering the reactor at $\tau_0 = 0$ does not exceed some value τ_i :

$$F(\tau_i) = P(\tau \leq \tau_i) \quad (9.1)$$

The properties of the above function are such that

$$F(\tau_2) \geq F(\tau_1)$$

if $\tau_2 > \tau_1$,

$$F(0) = 0,$$

$$\text{and } F(\infty) = 1$$

If τ is a continuous random variable, then $F(\tau)$ is a continuous function, and $dF(\tau)$ is the volumetric fraction of material in the reactor exit stream which has spent a time between τ and $d\tau$ within the reactor *.

The name 'differential distribution function' or 'distribution density function' is given to the derivative

$$dF(\tau)/d\tau = f(\tau)$$

Some of its properties are:

$$f(\tau) \geq 0 \quad (9.4)$$

$$f(0) = 0 \quad (9.5)$$

$$\int_0^{\infty} f(\tau) d\tau = 1 \quad (9.6)$$

The quantity $f(\tau)d\tau$ has the same physical meaning as $dF(\tau)$. For example, if τ_i is some specific residence time between τ and $\tau + d\tau$, then

$$f(\tau_i)d\tau = dF(\tau) = P(\tau \leq \tau_i \leq \tau + d\tau) \quad (9.7)$$

The probability that the residence time of a fluid element within the reactor falls within the finite interval from τ_1 to τ_2 is

$$P(\tau_1 \leq \tau \leq \tau_2) = \int_{\tau_1}^{\tau_2} f(\tau) d\tau = \int_{\tau_1}^{\tau_2} dF(\tau) = F(\tau_2) - F(\tau_1) \quad (9.8)$$

The probability that the residence time of the stream within the reactor is greater than some value τ is $1 - F(\tau)$ because

$$\int_{\tau}^{\infty} f(\tau) d\tau = \int_0^{\infty} f(\tau) d\tau - \int_0^{\tau} f(\tau) d\tau = 1 - F(\tau) \quad (9.9)$$

* It is termed the *external age distribution function* and given the symbol $E(t)dt$ by many authors. *Translator's note.*

In view of the residence time distribution functions (the internal age distribution or the external age distribution), the mean residence time of the stream within the reactor may be looked upon as the expected or mean value of a continuous random variable:

$$M(\tau) = \bar{\tau} = \lim_{N \rightarrow \infty} \sum_{i=1}^N \tau_i P(\tau = \tau_i) = \int_0^{\infty} \tau f(\tau) d\tau \quad (9.10)$$

9.2 Establishing the Residence Time Characteristics by Experiment

Experimentally, the residence time characteristics are established by what are called *stimulus-response techniques*. The stimulus is usually a change in concentration of a solute or tracer material in the feed stream to the system, with the tracer material usually differing from the feed stream in some property (colour, electrical conductivity, optical density, acidity, radioactivity, etc.). The tracer material should be such that it will not be changed or absorbed in the course of a test (say, due to a chemical reaction, adsorption or settling). Furthermore, it is desirable that the tracer material should readily be amenable to precise concentration measurements.

The stimulus may be a step change (no tracer is added at time $\tau_0 = 0$, while following that instant it is added at a constant rate), an impulse (a certain quantity of tracer is injected instantaneously into the feed stream), or a periodic change (for example, changing in a sinusoidal manner). The concentration or quantity of tracer is observed at the system outlet for a series of time intervals, and these data are plotted as curves.

The integral distribution function is established by applying a step change (Fig. 9.1). By measuring the tracer concentration C_t at the system outlet at time τ_i and relating it to the original concentration, $C_{t,0}$, we can find what fraction of tracer appears in the exit stream at the end of time τ_i , that is, what fraction of the stream has spent within the reactor a time

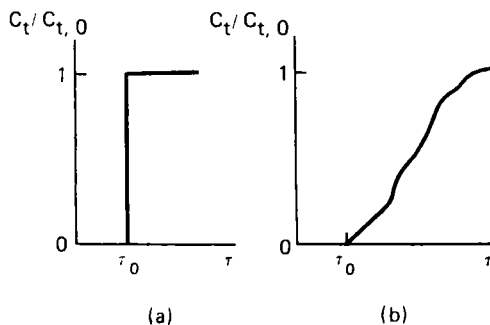


Fig. 9.1 Response to a step input:
a, stimulus; b, response (*F*-diagram)

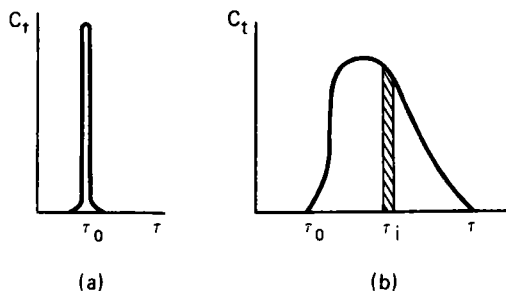


Fig. 9.2 Response to an impulse input:
a, stimulus; *b*, response (*C*-diagram)

shorter than τ_i . This dimensionless concentration

$$C_t(\tau)/C_{t,0} = C(\tau)$$

can vary from zero to unity. The function $C(\tau)$ has the same properties as the function $F(\tau)$, and the associated response curve is usually known as the *F*-diagram.

It is important to stress that the tracer resides in the reactor during the same time as the feed stream elements labelled with the tracer. Since $C(\tau)$ is a dimensionless quantity, it is the same for both the tracer and the labelled feed stream.

The differential distribution function $f(\tau)$ corresponds to the response to an impulse stimulus (Fig. 9.2). Let us prove the point.

Let at time $\tau_0 = 0$ a tracer quantity $n_{t,0}$ be injected instantaneously into the feed stream entering a continuous reactor. At some other time, τ_i , the tracer concentration at the exit from the reactor will be $C_t(\tau_i)$, and the product $vC_t(\tau_i)$, where v is the volumetric throughput (or flow rate), will be equal to the flow rate of the tracer with the exit stream. If we consider the situation at two instants, τ_i and $\tau_i + d\tau$, differing by an infinitesimal time span $d\tau$, the product $vC_t(\tau_i)d\tau$ will show the quantity of tracer leaving the reactor during the time interval between τ_i and $\tau_i + d\tau$. On dividing this quantity by $n_{t,0}$ we will find what fraction of the original quantity of tracer has spent within the reactor the time from τ_i to $\tau_i + d\tau$: $C_t(\tau_i)v d\tau / n_{t,0}$. By definition, this fraction is equal to $dF(\tau)$ or $f(\tau)d\tau$, see Eq. (9.7). Hence,

$$C_t(\tau)v/n_{t,0} = f(\tau) = dF(\tau)/d\tau \quad (9.12)$$

If v is constant and $n_{t,0}$ is constant in accord with the impulse injection of the tracer, it follows that the function $C_t(\tau)$ is the same as the function $f(\tau)$ up to the constant. This is the reason why we can establish the differential distribution function by measuring the tracer concentration at a series of time intervals. A plot of the above relation is usually referred to as the *C*-diagram.

As with the integral distribution function, $C_t(\tau)$ tells us for how long the fluid elements labelled with the tracer have stayed within the reactor.

Now let us take a look at the distribution functions for reactors with the ideal flow patterns (perfect mixing and plug flow), and for reactors described by the cascaded and dispersion models.

9.3 The Residence Time Distribution Functions for Ideal and Non-Ideal Continuous Flow Reactors

The well-stirred tank reactor. We set out to derive the equation that will enable us to calculate the integral distribution function $F(\tau)$ for a well-stirred tank reactor under steady-state conditions, then to differentiate that function in order to obtain the differential distribution functions $f(\tau)$.

Under the assumptions of an ideal flow pattern, any fluid element entering a perfectly mixed reactor may appear at any point within the reactor or in the exit stream right after it has entered the reactor. In consequence, the probability of this fluid element leaving the reactor is independent of its path or of its age (that is, the time during which it has stayed within the reactor). Therefore the probability that it will stay in the vessel longer than the time $\tau + \Delta\tau$ is the combination of the probabilities of two independent events:

- (1) The residence time is greater than τ .
- (2) The residence time is greater than $\Delta\tau$.

The probability of the first event is $1 - F(\tau)$; the probability of the second event is $1 - F(\Delta\tau)$. The probability of simultaneous occurrence of two independent events is equal to the product of the individual probabilities

$$1 - F(\tau + \Delta\tau) = [1 - F(\tau)][1 - F(\Delta\tau)] \quad (9.13)$$

or

$$1 - F(\tau + \Delta\tau) = 1 - F(\tau) - F(\Delta\tau) + F(\tau)F(\Delta\tau) \quad (9.14)$$

Because

$$\Delta F(\tau) = F(\tau + \Delta\tau) - F(\tau) \quad (9.15)$$

it follows that

$$\Delta F(\tau) + F(\tau)F(\Delta\tau) = F(\Delta\tau) \quad (9.16)$$

By definition, $F(\Delta\tau)$ is the volumetric fraction of material in the reactor exit stream that has spent within the reactor a time less than $\Delta\tau$. The volume of material leaving the reactor in the meantime will be $v\Delta\tau$. The probability of leaving the reactor is the same for all fluid elements within a perfectly mixed reactor. Therefore,

$$F(\Delta\tau) = v\Delta\tau / V = \Delta\tau / \bar{\tau} \quad (9.17)$$

where

$$\bar{\tau} = V/v$$

is the mean residence time.

On substituting $F(\Delta\tau)$ into Eq. (9.16) with $\Delta\tau$ tending to $d\tau$, we obtain a differential equation of the form

$$dF(\tau)/d\tau + (1/\bar{\tau})F(\tau) = 1/\bar{\tau} \quad (9.18)$$

which can be solved on assuming that the initial condition is

$$F(0) = 0 \quad (9.19)$$

Equation (9.18) is a 1st-order differential equation with variables separable. It may be re-cast as follows:

$$dF(\tau)/[1 - F(\tau)] = (1/\bar{\tau})d\tau \quad (9.20)$$

On integrating Eq. (9.20), we get

$$-\ln [1 - F(\tau)] = \tau/\bar{\tau} + \ln M \quad (9.21)$$

where M is the constant of integration. On re-arranging, Eq. (9.21) finally takes the form

$$1 - F(\tau) = (1/M) \exp (-\tau/\bar{\tau})$$

or

$$F(\tau) = 1 - (1/M) \exp (-\tau/\bar{\tau}) \quad (9.22)$$

In accord with the initial condition, Eq. (9.19), the integration constant is $M = 1$. Finally, we get

$$F(\tau) = 1 - \exp (-\tau/\bar{\tau}) \quad (9.23)$$

The residence time distribution density $f(\tau)$ may be found by differentiating Eq. (9.23):

$$f(\tau) = dF(\tau)/d\tau = (1/\bar{\tau}) \exp (-\tau/\bar{\tau}) \quad (9.24)$$

The integral distribution function $F(\bar{\tau})$ and the differential distribution function $f(\bar{\tau})$ for the residence time in a continuous flow well-stirred tank reactor are shown in the plots of Fig. 9.3.

The plug flow tubular reactor. With a flat velocity profile, all fluid elements must stay in the reactor precisely the same time equal to the mean residence time

$$\bar{\tau} = V/v$$

In consequence, for any $\tau < \bar{\tau}$,

$$F(\tau) = 0$$

and for any $\tau \geq \bar{\tau}$,

$$F(\tau) = 1$$

Thus, the integral distribution function $F(\tau)$ for a plug flow tubular reactor is a discontinuous function which takes on only two values, namely 0 and 1 (Fig. 9.4a).

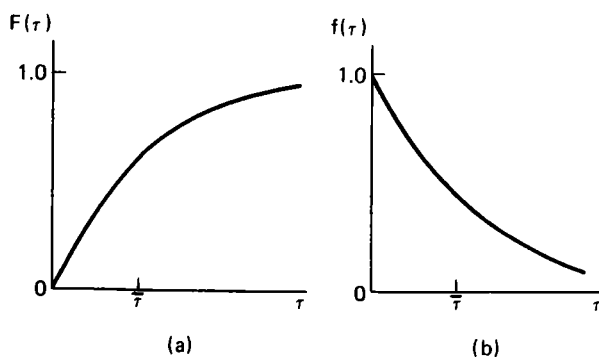


Fig. 9.3 (a) Integral and (b) differential residence time distribution functions for a continuous perfectly mixed reactor

The differential distribution function can be obtained by differentiating $F(\tau)$. The derivative of a discontinuous function has the special name of *Dirac's delta-function*, $\delta(\tau - \bar{\tau})$, whose plot is shown in Fig. 9.4b. Thus,

$$f(\tau) = dF(\tau)/d\tau = \delta(\tau - \bar{\tau}) \quad (9.25)$$

Dirac's delta function has several specific properties:

(1) The value of the function $\delta(\tau - \bar{\tau})$ is zero for all values of $\tau < \bar{\tau}$ and $\tau > \bar{\tau}$.

(2) When $\tau = \bar{\tau}$,

$$\delta(\tau - \bar{\tau}) = \delta(0) = \infty \quad (9.26)$$

(3) The delta function must satisfy the condition

$$\int_{-\infty}^{+\infty} \delta(\tau - \bar{\tau}) d\tau = 1 \quad (9.27)$$

Since negative values of τ have no physical meaning, the lower limit of in-

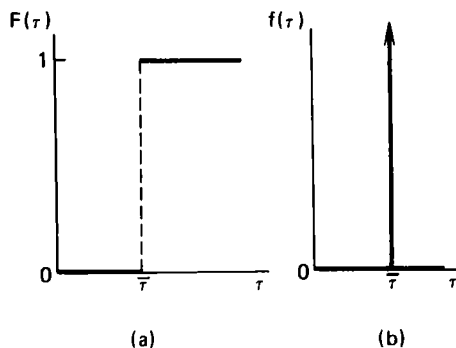


Fig. 9.4 (a) Integral and (b) differential residence time distribution functions for a continuous plug flow reactor

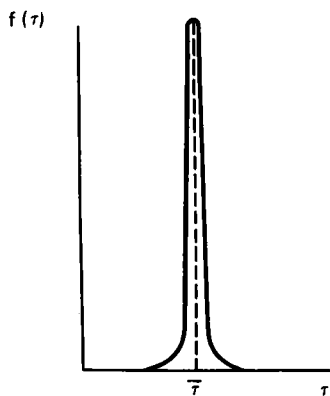


Fig. 9.5 Approximation to Dirac's delta-function

tegration in Eq. (9.27) may be replaced with $\tau = 0$. Then the equation

$$\int_0^{\infty} \delta(\tau - \bar{\tau}) d\tau = 1 \quad (9.28)$$

checks with one of the properties of the differential distribution functions, see Eq. (9.6).

Of course, the Dirac delta-function is an idealization, as is in fact the plug flow model to describe which it may be used. We may plot a function similar to $\delta(\tau - \bar{\tau})$; it is shown in Fig. 9.5. As the area between the left and right sides of the plot grows narrower, its height must be increased so that the area it encloses (that is, the integral) could retain its value of 1. Notably, this will be the shape of the differential distribution function for the residence time in a non-ideal tubular reactor in which the flow pattern approaches the plug flow.

The cascade of ideal stirred-tank reactors (the cascaded model). The form of the distribution function for a cascade of ideal stirred-tank reactors may be found by using the analogy between the distribution functions and the response diagrams*.

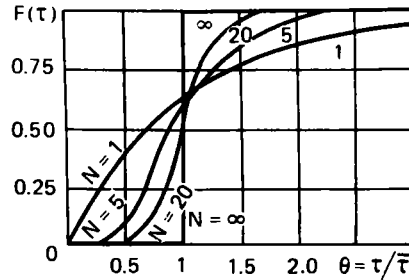
The function corresponds to the relation

$$C(\tau) = C_t(\tau)/C_{t,0}$$

which is the response to a step input of the tracer material. Suppose that starting at time $\tau_0 = 0$ an amount of tracer material with a constant concentration $C_{t,0}$ is injected into the stream entering the first reactor in the cascade. After tracer injection the reaction system will be under unsteady-

* Using this approach, we may also find the shape of the distribution function for a single ideal stirred-tank reactor.

Fig. 9.6 Integral residence time distribution function for the cascaded model with several values of N



state (or transient) conditions. This system may be described by writing a material balance on the tracer, recalling that it is not used up in the chemical reaction. The quantity of tracer entering the n th stage of the cascade over time $d\tau$ is $vC_{t,n-1}d\tau$. The quantity of tracer material leaving the same stage is $vC_{t,n}d\tau$. The change in tracer quantity will then be

$$d(V_n C_t) = V_n dC_t$$

The material balance on the tracer material takes the form

$$v(C_{t,n-1} - C_{t,n})d\tau = V_n dC_t \quad (9.29)$$

If all the stages in a cascade have the same volume, the mean residence time in a cascade of N stages will be

$$\bar{\tau} = NV_n/v \quad (9.30)$$

and the mean residence time in the n th stage will be

$$\bar{\tau}_n = \bar{\tau}/N = V_n/v \quad (9.31)$$

In view of Eq. (9.31), we may re-cast Eq. (9.29) as

$$dC_t/d\tau + (N/\bar{\tau})C_t = (N/\bar{\tau})C_{t,n-1} \quad (9.32)$$

By solving the above equation consecutively, first for the 1st stage of the cascade subject to the initial condition $C_t = 0$ if $\tau = 0$; then for each successive stage, we can obtain the relation $C_t(\tau)$ and, as a consequence, the integral distribution function as a series of the form

$$F(\tau) = C_t(\tau)/C_{t,0} = 1 - \exp(-N\tau/\bar{\tau}) \left[1 + N\tau/\bar{\tau} + \frac{1}{2!} (N\tau/\bar{\tau})^2 + \dots + \frac{1}{(N-1)!} (N\tau/\bar{\tau})^{N-1} \right] \quad (9.33)$$

The integral distribution functions for a cascade of N identical ideal stirred-tank stages (for the cascaded model of a continuous flow reactor with N as parameter) for several values of N are plotted in Fig. 9.6.

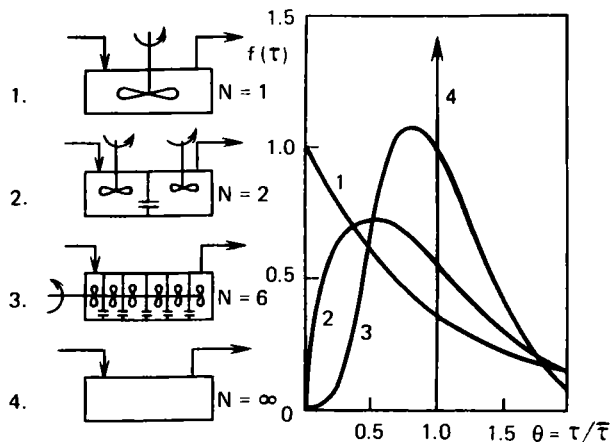


Fig. 9.7 Differential residence time distribution function for the cascaded model with several values of N

By differentiating $F(\tau)$, we can obtain the differential distribution function

$$f(\tau) = \frac{N^N}{(N-1)!} \left(\frac{\tau}{\bar{\tau}}\right)^{N-1} \exp(-N\tau/\bar{\tau}) \quad (9.34)$$

The differential distribution functions for the cascaded model at several values of N are plotted in Fig. 9.7. In the discussion of the cascaded model it was noted that this model can be used to describe both the continuous flow well-stirred tank reactor and the continuous plug flow tubular reactor. To demonstrate, at $N = 1$ Eq. (9.31) reduces to Eq. (9.24) applicable to an ideal stirred-tank reactor, while at N tending to infinity,

$$\lim f(\bar{\tau}) = \delta(\tau - \bar{\tau})$$

Eq. (9.31) is the distribution function for a plug flow tubular reactor.

Thus, after the response diagram of a reactor with a real flow pattern has been found by experiment, we may compare it with the design curves for the cascaded model and determine the model parameter N .

It is to be remembered that when the cascaded model is used in the design of real chemical reactors, the parameter N should be found from the response diagram obtained in a reaction vessel similar in its flow pattern to the reactor being designed.

The dispersion model. As with the cascaded model, the derivation of the residence time distribution function for reactors described by a one-parameter dispersion model is likewise based on the tracer concentration in the exit stream. To this end, we should first solve the differential equation describing the dispersion model under unsteady-state conditions without a

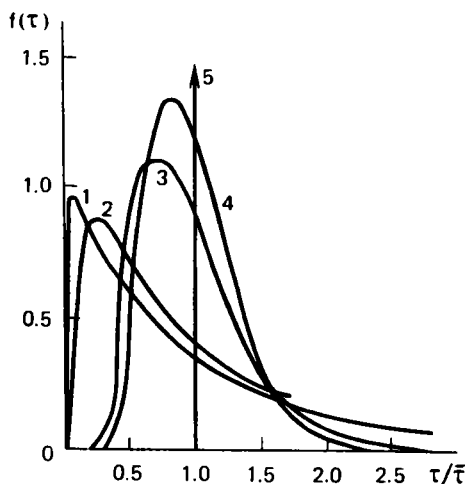


Fig. 9.8 Differential residence time distribution function for the dispersion model at several values of the Peclet number ($Pe = uL/D_L$):

1, $Pe = 0.1$; 2, $Pe = 1$; 3, $Pe = 10$;
4, $Pe = 17.8$; 5, $Pe = \infty$

chemical reaction.

$$\partial C_i / \partial \tau = -u(\partial C_i / \partial z) + D_L(\partial^2 C_i / \partial z^2) \quad (9.35)$$

On introducing the dimensionless concentration $C = C_i / C_{i,0}$, the dimensionless time $\theta = \tau / \bar{\tau}$ and the dimensionless distance $l = z / L$, and recalling that $\bar{\tau} = V/v = L/u$, we may re-cast Eq. (9.35) in dimensionless form as

$$(u/L)(\partial C / \partial \theta) = -(u/L)(\partial C / \partial l) + D_L(\partial^2 C / L^2 \partial l^2)$$

or as

$$\partial C / \partial \theta = -\partial C / \partial l + (1/Pe)(\partial^2 C / \partial l^2) \quad (9.36)$$

The final solution of Eq. (9.36) has the form

$$C = C_{i,L} / C_{i,0} = (Pe/\pi\theta)^{1/2} \exp [-Pe(1 - \theta)^2/4\theta] \quad (9.37)$$

The differential distribution functions $f(\tau)$ of the dispersion model for several values of the Peclet number are plotted in Fig. 9.8.

From comparison of Fig. 9.7 and Fig. 9.8 it is seen that the distribution function of the cascaded model at $N = 1$ is practically identical with the distribution curve of the dispersion model with Pe tending to zero, and at large values of N with curves for which $Pe \gg 1$. This result is only too natural because the dispersion model and the cascaded model are simply various approximations to the same real process.

It can be shown that the distribution function for the cascaded model may be used to describe processes answering the one-parameter dispersion model. If $uL/D_L = Pe > 10$, the following approximate equality

$$Pe/2 \approx N \quad (9.38)$$

is satisfied.

9.4 The Use of Residence Time Distribution Functions in the Design of Reactors with Segregated Streams

When unsegregated, a liquid consists of free individual molecules moving in all directions, colliding and mixing with all other molecules of the liquid — this is the *microstate* of the liquid.

When segregated, a liquid consists of globules each of which may be treated as a kind of microscopic batch-type reactor. This is the *macrostate* of the liquid.

When a reaction system consists of a huge number of globules each of which contains a very great number of molecules, the system is said to be in a *segregated state*. The outer envelope of a globule serves to retain its identity. The term 'segregated' also applies to any stream of solid particulate material where each grain may be regarded as an individual globule. Globules may also be found in liquids. Most often real liquids are only partly segregated.

A segregated liquid and an unsegregated liquid are compared in Fig. 9.9.

Now let us see how we should go about designing reactors with a segregated flow pattern.

Reactors with a segregated liquid stream. If we regard each globule in a segregated stream as a batch-type microscopic reactor of its own, the process taking place in the vessel as a whole can be evaluated by averaging the behaviour of the individual microscopic reactors.

With an isothermal reactor, the degree of chemical conversion within each globule depends on its residence time in the vessel. If this time differs from one globule to another, the degree of conversion will likewise be different for different globules. If the residence time of all the globules is the same, analysis of the chemical process in one globule will yield the same results as the analysis of the vessel as a whole. This condition holds for any batch-type reactor and for the plug flow tubular reactor.

For the other types of continuous flow reactors the residence time may vary between broad limits; it is given by the distribution function $F(\tau)$ or

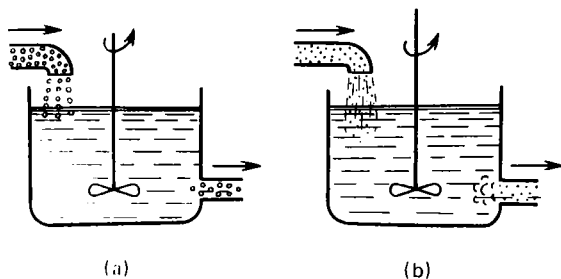


Fig. 9.9 (a) A segregated and (b) an unsegregated fluid flow through a reactor

$f(\tau)$. Let the number of globules leaving a continuous flow reactor per unit time be N and also recall that in the general case the residence time is different for different globules (except the plug flow tubular reactor). The fraction of globules which stay in the vessel from time τ_i to time $\tau_i + \Delta\tau$ is $f(\tau_i)\Delta\tau$. The degree of conversion of the reactant in a globule during time τ_i is decided by the kinetics of the chemical reaction. Suppose that the fraction of the reactant that did not react during the same time is

$$C_A(\tau_i)/C_{A,0} = 1 - x_A(\tau_i)$$

On adding together the fractions of unreacted reactant for each group of globules differing in age (that is, in the span of time spent in the reactor) and applying their statistical weights, we obtain the mean fraction of unreacted reactant in the exit stream. It should be remembered that the residence time may range from zero to infinity.

$$\begin{aligned} 1 - \bar{x}_A = \bar{C}_A/C_{A,0} &= \lim_{\Delta\tau \rightarrow 0} \sum_{\tau_i=0}^{\tau_i=\infty} [1 - x_A(\tau_i)]f(\tau_i)\Delta\tau \\ &= \int_0^{\infty} [1 - x_A(\tau)]f(\tau)d\tau = \int_0^{\infty} [C_A(\tau)/C_{A,0}]f(\tau)d\tau \end{aligned} \quad (9.39)$$

where:

$\bar{x}_A$ = mean fractional conversion of the reactant

$\bar{C}_A$ = mean concentration of the reactant in the exit stream

Equation (9.39) applies to the general case. In special cases we should use the differential distribution function $f(\tau)$ in a form decided by the prevalent flow pattern in the reactor, and the relation $1 - x_A(\tau)$ or $C_A(\tau)$ in a form decided by the rate equations for the reaction system in question.

For example, with a continuous flow well-stirred tank reactor, the function $f(\tau)$ has the form [see Eq. (9.24)]

$$f(\tau) = (1/\bar{\tau}) \exp(-\tau/\bar{\tau})$$

When a reactor is effecting a 1st-order reaction whose rate is given by

$$w_{rA} = -dC_A/d\tau = kC_A$$

we get for a batch-type reactor

$$C_A/C_{A,0} = \exp(-k\tau) \quad (9.40)$$

Then

$$1 - \bar{x}_A = (\bar{C}_A/C_{A,0}) \int_0^{\infty} \exp(-k\tau)(1/\bar{\tau}) \exp(-\tau/\bar{\tau})d\tau \quad (9.41)$$

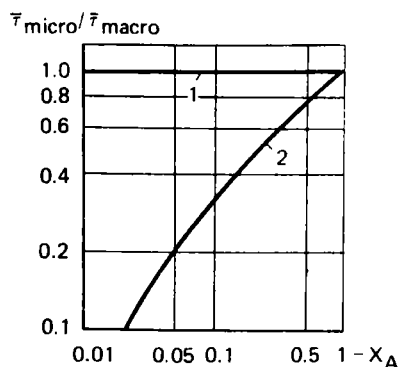


Fig. 9.10 Comparison of perfectly mixed reactor performance with the liquid stream in the microstate and the macrostate for (1) a first-order and (2) a second-order reaction

The value of the integral in Eq. (9.41) is

$$1 - \bar{x}_A = \bar{C}_A / C_{A,0} = 1/(1 + k\bar{\tau}) \quad (9.42)$$

It is to be noted that for a 1st-order reaction the above result does not differ from that obtained for a continuous flow well-stirred tank reactor without segregation. To demonstrate,

$$\bar{\tau} = (C_{A,0} - C_A)/kC_A$$

and

$$C_A / C_{A,0} = 1/(1 + k\bar{\tau}) \quad (9.43)$$

This finding applies, however, only to 1st-order reactions. In the case of a 2nd-order reaction, different results are obtained from analysis of a reactor with a segregated flow and a reactor in which the stream is in the state of microscopic mixing (the microstate). The final result of analysis for a segregated stream (without its derivation) takes the form

$$1 - \bar{x}_A = \bar{C}_A / C_{A,0} = \frac{\exp(1/k\bar{\tau}C_{A,0})}{k\bar{\tau}C_{A,0}} \text{ei}(1/k\bar{\tau}C_{A,0}) \quad (9.44)$$

where $\text{ei}(1/k\bar{\tau}C_{A,0})$ is an integral exponential function whose values are tabulated (see tables of definite integrals).

The behaviour of well-stirred tank reactors effecting 1st and 2nd order reactions, with the streams in the micro- and macro-states, is compared in graphical form in Fig. 9.10.

Reactors with a moving bed of particulate material. When dealing with binary heterogeneous systems, one of the two phases may be treated as a liquid in the macrostate. For example, when a process is effected in a gas-solid or a liquid-solid system, the solid particles are well-defined globules each of which contains a multitude of molecules and has abrupt boundaries.

In Chap. 4, we discussed the kinetics of heterogeneous noncatalytic processes in the gas-solid system for a case when the gaseous reactant passes over a single solid particle. Now we will consider a continuous flow reactor in which instead of a single solid particle a statistical population of solid particles is moving. In accord with the overall approach to segregated streams, each solid particle may be treated as a microscopic batch-type reactor. Then each particle taken separately should obey the kinetic relations derived in Chap. 4. If we know the residence time distribution of the solid particles, we are able to deduce the average characteristics at the exit from the reactor, using the equation

$$1 - \bar{x}_B = \int_0^{\infty} [1 - x_B(\tau)]f(\tau)d\tau \quad (9.45)$$

With heterogeneous reactors, however, we must take into account several further features of heterogeneous processes. Above all, it should be kept in mind that the specific form of the equation describing the relation between the fractional conversion x_B and the residence time of a solid particle in the reactor depends on which step controls the rate of the process. If the rate-controlling step under the specified process conditions (temperature, particle size, linear velocity of the gas, etc.) is known, the relation $x_B(\tau)$, as found by one of the equations (4.33), (4.43) or (4.52), should be substituted in Eq. (9.45). If, on the other hand, the heterogeneous process is effected in the transition region under the specified process conditions (that is, none of the steps is a rate-controlling one), the form of the function $x_B(\tau)$ can be determined, using relations similar to Eq. (4.22).

Another distinction of the analysis involving reactors which process particulate materials is that, given the same residence time, the degree of conversion will be different for any two solid particles differing in size. It follows from Eqs. (4.33), (4.43) and (4.52) that the time required to reach the same degree of conversion is proportional to the radius of the solid particle if the process takes place in the external diffusion or kinetic region, or even to R^2 if the rate-controlling step is pore diffusion.

As a rule, the solid phase consists of particles differing in size over some range of values of R . In consequence, when dealing with a heterogeneous process in a reactor, the results must be averaged not only over the residence time in accord with Eq. (9.45), but also over the range of solid particle sizes.

The size distribution of solid particles could be accounted for by using the distribution functions $F(R)$ or $f(R)$. For experimental purposes, however, it is customary to use sieve analysis which yields results in discrete form: the mass fraction of particles with a mean size $\bar{R}_i$ is $\varphi(\bar{R}_i)$; the frac-

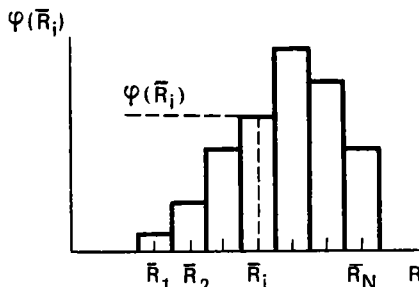


Fig. 9.11 Bar diagram showing particle size distribution in a solid feed

tion of particles with a mean size $\bar{R}_{i+1}$ is $\varphi(\bar{R}_{i+1})$, etc. The dimension $\bar{R}_1, \bar{R}_2, \dots, \bar{R}_i, \dots, \bar{R}_n$ is the mean size of the particles left on the sieve of a given mesh size. If, for example, a fine sieve has a mesh of radius R_i , and the next coarser sieve has a mesh of radius R_{i+1} , the mean size of the particles remaining on the fine sieve is the arithmetic mean of the two mesh sizes:

$$\bar{R}_i = (R_i + R_{i+1})/2 \quad (9.46)$$

If a sample taken for sieve analysis has a mass G and the mass of particles with a mean size $\bar{R}_i$ is $G(\bar{R}_i)$, the statistical weight of the fraction will be

$$\varphi(\bar{R}_i) = G(\bar{R}_i)/G \quad (9.47)$$

Naturally,

$$\sum_{i=1}^n \varphi(\bar{R}_i) = 1 \quad (9.48)$$

where $\bar{R}_n$ is the maximum particle size.

Proceeding from sieve analysis, it is assumed that the statistical weight of a given particle size in the stream of particulate material is the same as it is in the sample taken for the analysis. The discrete size distribution of the particles is presented as a table or as a bar diagram (Fig. 9.11).

Suppose that all particles differing in size stay in the reactor for a time τ . The particles of a smaller radius will achieve a higher degree of conversion than those of a larger radius.

The mean fraction of unreacted reactant, $1 - \bar{x}_B$, given the same residence time τ , can be found on taking the summation over the size

$$1 - \bar{x}_B = \sum_{R_i=0}^{R_{\max}} [1 - x_B(\bar{R}_i)]\varphi(\bar{R}_i) \quad (9.49)$$

where $0 \leq x_B \leq 1$. When taking the summation, it is important to remember that the residence time of very fine particles may prove sufficient for a complete conversion of the solid reactant B or that there is some

minimal size $R_{\min}$ for which the condition $\tau(R_{\min}) = \tau_{comp}$ is satisfied. Then all terms corresponding to the sizes $R_i \leq R_{\min}$ will vanish in Eq. (9.49), irrespective of their statistical weights. Therefore, when taking the summation, they may be dropped at the outset and Eq. (9.49) will then take the form

$$1 - \bar{x}_B = \sum_{R_{\min}(\tau=\tau_{comp})}^{R_{\max}} [1 - x_B(\bar{R}_i)] \varphi(\bar{R}_i) \quad (9.50)$$

Thus, using Eqs. (9.45) and (9.50), we can average the degree of conversion of a segregated stream over the residence time or over the particle size range. In the general case, however, the stream may also be described in terms of the residence time distribution. If this is the case, the first step should be to find the mean fractional conversion for each particle size by Eq. (9.45) subject to the form of the function $f(\tau)$. The second step is to take the summation over the size range in accord with Eq. (9.50), that is,

$$1 - \bar{x}_B = \sum_{R_i=0}^{R_{\max}} \left\{ \int_0^{\infty} [1 - x_B(\bar{R}_i, \tau)] f(\tau) d\tau \right\} \varphi(\bar{R}_i) \quad (9.51)$$

Chapter Ten

HEAT TRANSFER IN CHEMICAL REACTORS

Knowledge of the temperature distribution in a chemical reactor is extremely important in an analysis of the processes that take place in it because temperature is one of the key process variables. For one thing, temperature affects the state of chemical equilibrium and the maximum attainable (equilibrium) conversion of the reactants. For another, temperature affects reaction rate. Also, temperature has a direct bearing on the selectivity of a complex reaction. Changes in temperature may cause a heterogeneous process to move from the kinetic into the diffusion region or the other way around. A nonuniform temperature distribution in a reactor may bring about local heat build-ups, unwanted side reactions, etc.

The temperature in the reactor as a whole and its distribution may be caused to change by the heat released or absorbed during reactor processes and also by heat transfer between the reactor and the surroundings.

The temperature distribution in a reactor is also affected by the prevailing flow pattern. For example, in a well-stirred tank reactor all process variables, including temperature, are the same at any point within the reactor as they should be on the assumption of perfect mixing (see Sec. 7.1). On

the contrary, in a plug flow tubular reactor the temperature at one point may differ from that at any other. Agitation affects the specific rate of heat transfer in the reaction vessel.

A proper account of all thermal factors is taken by writing a heat balance over the reactor. With a non-isothermal reactor, one has to solve simultaneously the set of material and heat balances, with the first taking care of the changes in the mass of material and the second, of the change in the quantity of heat with the progress of the chemical process involved.

10.1 Heat Balance. Thermal Conditions of Chemical Reactors

A heat balance takes care of all heat flows entering and leaving a reactor. These flows are as follows.

Q_{in} refers to the sensible heat of the reaction mixture entering the element of volume over which the balance is written (the inlet or feed stream).

Q_{out} refers to the sensible heat of the reaction mixture leaving the same element of volume (the exit or outlet stream).

Q_r refers to the heat of reaction (the sign of this term depends on whether the reaction involved is endothermic or exothermic).

Q_t refers to the heat exchanged with the surroundings (heat may be transferred either from the reactor to a surrounding coolant or to the reactor from the surroundings, so the heat transport may be directed into or out of the element of volume).

Under steady-state conditions, the algebraic sum of all heat flows into and from the reactor is zero:

$$Q_{in} - Q_{out} \pm Q_r \pm Q_t = 0 \quad (10.1)$$

Under unsteady-state conditions, a positive or a negative accumulation of heat takes place in the selected element of volume:

$$Q_{in} - Q_{out} \pm Q_r \pm Q_t = Q_{acc} \quad (10.2)$$

Equations (10.1) and (10.2) are general heat balances over a chemical reactor. Each may take some specific form, depending on the flow pattern prevailing in the reactor and whether the reactor is effecting an isothermal, an adiabatic, or a non-isothermal, non-adiabatic (heat-regulated) process.

Isothermal operation. In this condition the temperature of the reaction mixture entering the reactor is equal to that of the mixture leaving the reactor. This can happen if the heat released or absorbed on reaction is fully balanced by heat exchanged with the surroundings. Given a system with constant physical properties and operating under steady-state isothermal conditions, we may write

$$Q_{in} = Q_{out} \quad (10.3)$$

$$|Q_r| = |Q_t| \quad (10.4)$$

Adiabatic operation. In this condition, there is no heat transfer to or from the surroundings. All of the heat of reaction is used up to heat or cool the reaction mixture. For adiabatic operation under steady-state conditions we may write

$$|Q_{in} - Q_{out}| = |Q_r| \quad (10.5)$$

Non-isothermal, non-adiabatic (heat-regulated) operation. In this condition, some of the heat of reaction is spent to change the heat content of (to heat or cool) the reaction mixture, and some is exchanged with the surroundings. This condition is encountered in real chemical reactors most often. It is described by the overall heat balance over a reactor, Eq. (10.1).

The mathematical models of isothermal reactors were examined in Chaps. 7 and 8. Analysis and design on the basis of such models needs only material balances. In the case of non-isothermal reactors, one has to solve a set of material and heat balances. What follows is an exposition of how to write appropriate mathematical models and how to use these models in the analysis and design of non-isothermal reactors differing in the flow pattern.

10.2 The Non-Isothermal Continuous Flow Well-Stirred Tank Reactor

In writing balances in such cases, the selected element of volume for a well-stirred tank reactor is assumed to be the entire reaction volume V . As measured over an element of time $d\tau$ and over the volume V , the respective heat flows will be

$$Q_{in} = v_0 c_{p,0} \rho_0 T_0 d\tau \quad (10.6)$$

$$Q_{out} = v c_p \rho T d\tau \quad (10.7)$$

$$Q_r = \Delta H_r V w_{r,j} d\tau \quad (10.8)$$

$$Q_t = K_t A_{ht} \Delta T_{ht} d\tau \quad (10.9)$$

where:

- c_p = mean heat capacity of the reaction mixture at constant pressure
- ρ = mean density of the reaction mixture
- ΔH_r = enthalpy change on reaction per mole of reactant
- K_{ht} = overall heat-transfer coefficient
- A_{ht} = heat-transfer surface area
- ΔT_{ht} = driving force of heat transfer (the mean difference in temperature between the reactor and the surroundings)

The subscript "0" designates the quantities associated with the inlet or feed stream, while the quantities without a subscript are associated with the reaction mixture staying in or leaving the reactor at a given instant.

The accumulation of heat in the reactor over the time $d\tau$ is equal to the change in the heat content of the reaction mixture:

$$Q_{acc} = d(V\rho c_p T) \quad (10.10)$$

In view of Eqs. (10.2) and (10.6) through (10.10), the unsteady-state heat balance has the form

$$v_0 c_{p,0} \rho_0 T_0 d\tau - v c_p \rho T d\tau - \Delta H_r w_{rA} V d\tau \pm K_{ht} A_{ht} \Delta T_{ht} d\tau = d(V\rho c_p T) \quad (10.11)$$

or

$$v_0 c_{p,0} \rho_0 T_0 - v c_p \rho T - \Delta H_r w_{rA} V \pm K_{ht} A_{ht} \Delta T_{ht} = V \frac{d(\rho c_p T)}{d\tau} \quad (10.12)$$

Under steady-state conditions, the right-hand side of Eq. (10.12) is equal to zero. Furthermore, if we assume that $v_0 = v$ and neglect the change in the mean heat capacity and density of the reaction mixture due to changes in the composition and temperature of the reaction mixture *, then for operation under steady-state conditions we may write

$$v c_p \rho (T_0 - T) - \Delta H_r w_{rA} V \pm K_{ht} A_{ht} \Delta T_{ht} = 0 \quad (10.13)$$

In addition to the heat balance, Eq. (10.13), the mathematical model of a non-isothermal well-stirred tank reactor includes the material balance

$$v(C_{A,0} - C_A) - w_{rA} V = 0 \quad (10.14)$$

Equations (10.13) and (10.14) are interrelated: both include the function $w_{rA}(C_A, T)$. The reaction rate w_{rA} is a function of both the reactant concentration (conversion) and temperature. The higher the temperature, the higher the reaction rate. Therefore, a higher degree of conversion would seem to be achieved at the same mean residence time $\bar{\tau}$. However, the increase in conversion automatically leads to a fall in the reaction rate. In a continuous flow reactor of a specified volume both the conversion and the temperature settle at values which satisfy both Eq. (10.13) and Eq. (10.14).

By simultaneously solving Eqs. (10.13) and (10.14) at specified values of $\bar{\tau} = V/v$ and T_0 , we can find the values of x_A and T that satisfy both equations. In the pages that follow we will analyse the likely solutions of the material and heat balances first for an adiabatic well-stirred tank reactor, then for a similar, but non-adiabatic reactor. Using the results of this analysis, it will be possible to choose the values of process variables that would assure a high level of reactant conversion.

* This is a legitimate assumption if the temperature changes within a narrow range and no phase transformations take place in the reaction system.

Simultaneous solution of steady-state material and heat balances over an adiabatic continuous-flow well-stirred tank reactor. The mathematical model of an adiabatic continuous flow well-stirred tank reactor is a set of material and heat balances

$$\left. \begin{aligned} v(C_{A,0} - C_A) - w_{rA}V &= 0 \\ vC_p\rho(T_0 - T) - \Delta H_r w_{rA}V &= 0 \end{aligned} \right\} \quad (10.15)$$

Using the above set of equations, let us find the fractional conversion x_A and the temperature T achieved in the reactor. The solution actually obtained will depend on the specific form of the rate equation

$$w_{rA} = w_{rA}(C_A, T)$$

applicable to the reaction effected in a given reactor. To begin with, we will examine the solutions for kinetically simple reactions, namely the irreversible 1st-order reaction $A \rightarrow R$ and the reversible 1st-order reaction $A \rightleftharpoons R$ because the mathematics involved is the simplest in these cases.

As a first step, we re-arrange Eqs. (10.15). In the material balance we replace the change in concentrations, $(C_{A,0} - C_A)$, with an equal term, $C_{A,0}x_A$. As a second step, we simplify the heat balance by eliminating the reaction rate w_{rA} . To do this, we use the material balance in accord with which

$$w_{rA}V = v(C_{A,0} - C_A) = vC_{A,0}x_A$$

Then the heat balance takes the form

$$vC_p\rho(T_0 - T) - \Delta H_r vC_{A,0}x_A = 0$$

As a result of these manipulations, we may re-cast Eqs. (10.15) as

$$vC_{A,0}x_A - w_{rA}V = 0 \quad (10.16)$$

$$vC_p\rho(T_0 - T) - \Delta H_r vC_{A,0}x_A = 0 \quad (10.17)$$

The irreversible 1st-order reaction. The applicable rate equation takes the form

$$w_{rA} = kC_A = kC_{A,0}(1 - x_A) = k_0 \exp(-E/RT)C_{A,0}(1 - x_A) \quad (10.18)$$

On substituting it into Eq. (10.16), we get

$$vC_{A,0}x_A - k_0 \exp(-E/RT)C_{A,0}(1 - x_A)V = 0 \quad (10.19)$$

In order to find x_A and T , the material balance, Eq. (10.19), should be solved simultaneously with the heat balance, Eq. (10.17). An analytical solution of this system of equations is difficult to obtain because T appears in the equations both as a linear term and as part of the group which is the exponent. Such equations are transcendental and can only be solved by numerical methods.

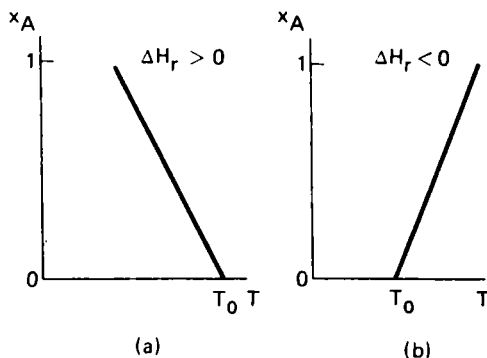


Fig. 10.1 Heat balance over a perfectly mixed reactor as an x_A -vs- T plot for (a) an endothermic and (b) an exothermic reaction

Let us solve Eqs. (10.17) and (10.19) graphically. To do this, we write the two equations as the functions $x_A(T)$, construct their plots and locate their intersections — they satisfy the two equations and are thus their solutions.

In the heat balance, Eq. (10.17), x_A is a linear function of T *:

$$x_A = (c_p \rho / C_{A,0} \Delta H_r)(T_0 - T) \quad (10.20)$$

The straight line described by Eq. (10.20) intersects the temperature axis at point $T = T_0$ and its slope is

$$b = -c_p \rho / C_{A,0} \Delta H_r \quad (10.21)$$

The sign of the slope depends on that of the enthalpy change — it is negative for endothermic reactions in which case $\Delta H_r > 0$ (Fig. 10.1a), and positive for exothermic reactions in which case $\Delta H_r < 0$ (Fig. 10.1b). The slope can be varied by varying the initial concentration $C_{A,0}$. If we assume that $x_A = 1$ (which implies that the reaction is carried to completion), it follows from Eq. (10.20) that

$$T_0 - T_{x_A=1} = \Delta T_{ad} = C_{A,0} \Delta H_r / c_p \rho \quad (10.22)$$

Here ΔT_{ad} is the maximum change in the temperature of the reaction mixture that can happen under adiabatic conditions, or the *adiabatic change of temperature* (for exothermic reactions, say, this will be an adiabatic heat build-up). On taking into account ΔT_{ad} , we may re-cast Eq. (10.20) as

$$x_A = T_0 / \Delta T_{ad} - (1 / \Delta T_{ad}) T \quad (10.23)$$

The form of the function $x_A(T)$ corresponding to the material balance, Eq. (10.19), depends on the type of rate equation that describes the reac-

* It should be remembered that we have assumed that c_p , ρ and ΔH_r are independent of temperature. If we consider the slight temperature dependence of these quantities, there will be some departure from linearity.

tion involved. For an irreversible 1st-order reaction (both exothermic and endothermic), the material balance, Eq. (10.19), may be written (recalling that $V/v = \bar{\tau}$) as

$$x_A = 1/[1/(k\bar{\tau}) + 1] = 1/[(1/k_0\bar{\tau}) \exp(E/RT) + 1] \quad (10.24)$$

Equation (10.24) describes a monotonically increasing function, $x_A(T)$. At low temperatures when the kinetic energy of molecules is substantially smaller than the activation energy (which can be concluded from comparing E and RT), the fractional conversion x_A tends to zero. At high temperatures when E and RT are of the same order of magnitude, the numerical values of $\exp(-E/RT)$ are small. Since the frequency (or pre-exponential) factor k_0 is anywhere between 10^8 and 10^{13} , it follows that x_A tends now to unity.

Thus, the plot of the function defined in Eq. (10.24) is a smooth curve (that is, one without positive or negative peaks) (curve 1 in Fig. 10.2) which asymptotically approaches zero at low temperatures and unity at high temperatures, but it has a single point of inflection at medium temperatures; its coordinates can be obtained by equating the derivative d^2x_A/dT^2 to zero.

The position that the middle region of the curve takes up relative to the temperature axis can be changed by increasing or decreasing the mean residence time $\bar{\tau}$ ($\bar{\tau} = V/v$). It follows from Eq. (10.24) that, given the same temperature, an increase in $\bar{\tau}$ leads to an increase in x_A (curve 2 in Fig. 10.2).

The solutions of the material and heat balances have a somewhat different form for endothermic and exothermic irreversible reactions. When an adiabatic well-stirred tank reactor effects an irreversible endothermic reaction, the plots of the functions defined by Eqs. (10.23) and (10.24)

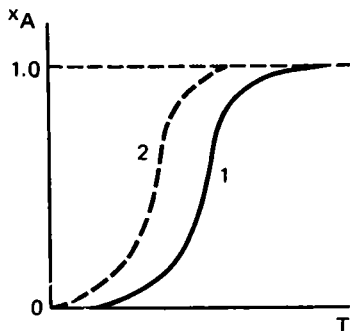


Fig. 10.2 Material balance over a perfectly mixed reactor as an x_A -vs- T plot for an irreversible 1st-order reaction at two values of mean residence time:

1, τ_1 ; 2, $\tau_2 > \tau_1$

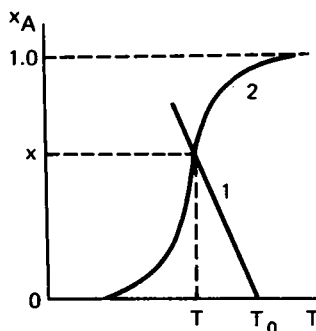


Fig. 10.3 Graphical solution of (1) the heat balance and (2) the material balance over an adiabatic perfectly mixed reactor effecting an irreversible endothermic reaction

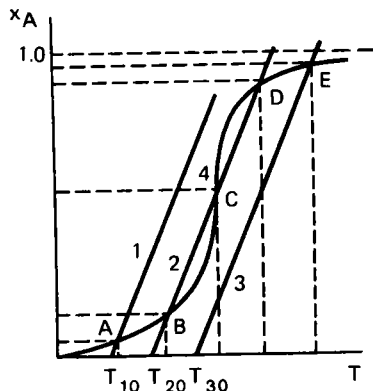


Fig. 10.4 Graphical solution of the heat balances (1, 2, 3) and the material balance (4) over an adiabatic perfectly mixed reactor effecting an irreversible exothermic reaction

have only one intersection (Fig. 10.3). The coordinates (x_A, T) of this intersection are the solution of the equations: If an adiabatic well-stirred tank reactor of a specified volume V receives a feed reactant A of initial concentration $C_{A,0}$ at a volumetric flow rate v and at an initial temperature T_0 , the irreversible endothermic reaction will proceed in the vessel at a temperature T , and the fractional conversion thus obtained will be x_A .

If an adiabatic reactor effects an irreversible exothermic reaction, the system of material and heat balances may have one or several solutions under steady-state conditions.

It is seen from Fig. 10.4 that the plots of the functions defined by Eqs. (10.23) and (10.24) have only one intersection if the initial temperature T_0 of the reaction stream is relatively low (say, T_{10}) or relatively high (say, T_{30}). It turns out then that when the feed is admitted at a low initial temperature T_{10} , the process would proceed at a temperature which only slightly differs from T_{10} and the associated fractional conversion (the ordinate of point A in Fig. 10.4) would likewise be very low. It is more attractive to operate the reactor at T_{30} . As before, the plots of the functions will intersect at a single point (point E), which means that the system of equations has only one solution, but the fractional conversion will be very high, being close to unity.

If, on the other hand, the feed is admitted to the reactor at T_{20} , the plots of the material and heat balances will intersect at three points, B , C , and D . The coordinates of these points are the solutions of the equations that make up the mathematical model of an adiabatic well-stirred tank reactor. It is said then that the reactor has a multiplicity of steady states. This situation involves the problem of steady-state stability (see Sec. 10.5).

The reversible 1st-order reaction. For a reversible 1st-order reaction of the form $A \rightleftharpoons R$ the rate equation

$$w_{rA} = k_1 C_A - k_2 C_R \quad (10.25)$$

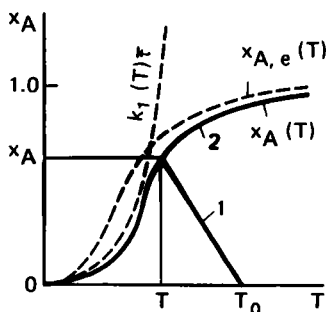


Fig. 10.5 Graphical solution of (1) the heat balance and (2) the material balance over an adiabatic perfectly mixed reactor effecting a reversible endothermic reaction

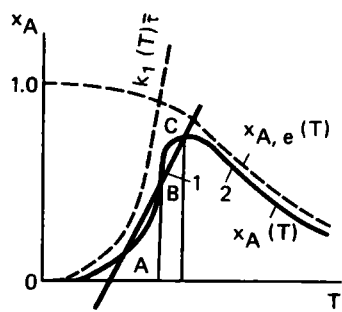


Fig. 10.6 Graphical solution of (1) the heat balance and (2) the material balance over a perfectly mixed adiabatic reactor effecting a reversible exothermic reaction

On expressing the concentrations C_A and C_R in Eq. (10.25) in terms of $C_{A,0}$ and x_A , we get

$$w_{rA} = k_1 C_{A,0} (1 - x_A) - k_2 C_{A,0} x_A = k_1 C_{A,0} \left(1 - \frac{k_1 + k_2}{k_1} x_A \right) \quad (10.26)$$

At equilibrium, the rate of the forward reaction in a reversible 1st-order reaction is equal to that of the reverse reaction:

$$k_1 C_{A,0} (1 - x_{A,e}) = k_2 C_{A,0} x_{A,e}$$

Hence it follows that

$$x_{A,e} = k_1 / (k_1 + k_2) \quad (10.27)$$

In view of Eq. (10.27), the rate equation of a reversible 1st-order reaction takes the form

$$w_{rA} = k_1 C_{A,0} (1 - x_A / x_{A,e}) \quad (10.28)$$

On substituting Eq. (10.28) into Eq. (10.16), the material balance may be re-cast as the temperature dependence of x_A :

$$x_A = 1 / (1/k_1 \tau + 1/x_{A,e}) \quad (10.29)$$

As should be expected, at $x_{A,e} = 1$ (that is, when the reaction becomes an irreversible 1st-order one), Eq. (10.29) reduces to Eq. (10.24).

In order to solve the system of material and heat balances for a reversible reaction graphically, we should construct a plot of the function defined by Eq. (10.29). The heat balance, Eq. (10.20), does not contain any kinetic reaction parameters, and its plot is independent of the form taken by the rate equation.

In Eq. (10.29), the temperature-dependent terms are the rate constant k_1 for the forward reaction and the equilibrium conversion $x_{A,e}$. In the case

of a reversible endothermic reaction ($\Delta H_r > 0$), an increase in temperature brings on an increase in the rate constant and the equilibrium conversion. When computed by Eq. (10.29), x_A will have a lower value at any temperature than $k_1\bar{\tau}$, and a lower value than $x_{A,e}$. In other words, the plot of the function $x_A(T)$ should lie in a coordinate plane (Fig. 10.5) below the plots of $k_1(T)\bar{\tau}$ and $x_{A,e}(T)$.

The set of material and heat balances for a reversible exothermic reaction has the same form as it has for a reversible endothermic reaction — that is, they are Eqs. (10.29) and (10.20). However, the function $x_A(T)$ defined by Eq. (10.29) yields a different plot. This is because the equilibrium conversion $x_{A,e}$ decreases with increasing temperature in the case of exothermic reactions. Therefore, on constructing a plot of $x_A(T)$ and performing the same manipulation as in the case of the reversible endothermic reaction, we obtain a curve with a peak (Fig. 10.6). The absolute value and position of the peak relative to the curve are determined by the mean residence time $\bar{\tau}$, on the one hand, and by the state of chemical equilibrium, on the other.

In Fig. 10.6, the heat balance is represented by straight line 1 which has a positive slope. This line may intersect curve 2 representing the material balance at one or several points, thus implying that there may be one or several steady states.

Enhancing the conversion of reactants in an adiabatic well-stirred tank reactor. Depending on the initial conditions (the inlet temperature T_0 , the initial concentration $C_{A,0}$), the mean residence time ($\bar{\tau} = V/\nu$), and the type of chemical reaction, a continuous flow well-stirred tank reactor finally attains a steady state where the temperature of the reaction mixture and the conversion at the exit from the reactor remain unchanged with time. The respective values of T and x_A may be found by simultaneously solving the material and heat balances, as has been shown previously.

A major objective of any industrial-scale process is to achieve the maximum attainable conversion of the feedstock. The process conditions in which this goal can be achieved in an adiabatic well-stirred tank reactor can be deduced from an analysis of the solutions of the material and heat balances.

A graphical solution of the material and heat balances reduces to locating the intersection between the plots of the functions $x_A(T)$ answering the two equations. On these plots (see Figs. 10.3 through 10.6), a higher degree of conversion in an adiabatic reactor is achieved when the intersection is shifted into the region of higher values of x_A . This shift can be brought about by changing the relative position of the plots representing the material and heat balances. This can be done in more than one way as follows.

With endothermic reactions (both irreversible and reversible), the conversion can be enhanced above all by raising the initial temperature T_0 — this will cause line 1 to move parallel to itself to the right (see Figs. 10.3 and 10.5).

With irreversible exothermic reactions, a rise in the inlet temperature will likewise bring about an increase in conversion (see line 3 in Fig. 10.4). At the same time, this will avoid a triple intersection between lines 2 and 4, which occurs when there is a multiplicity of steady states. However, any increase in the initial temperature must be justified economically — the increased conversion will be accompanied by increased expenses on pre-heating the reaction mixture.

With reversible exothermic reactions effected in an adiabatic well-stirred tank reactor, efforts should be made so that the solution of the material and heat balances yields a peak on line 2 representing the material balance (see Fig. 10.6). The shift of line 1 in response to an increase in the initial temperature might bring on a fall rather than a rise in conversion. For these and some other reasons, the choice of optimal process conditions for reversible exothermic reactions is especially challenging.

Alternatively, the position of the plot representing the heat balance may be changed by changing its slope. The slope

$$\tan \alpha = -c_p \rho / C_{A,0} \Delta H_r$$

of the line described by Eq. (10.20) may be increased or decreased by changing the initial concentration $C_{A,0}$. With endothermic reactions, x_A can be increased while maintaining the initial temperature at its previous value by increasing its slope. This could be done by decreasing $C_{A,0}$, but this is not always attractive because a feed low in reactants would have then to be used. An increase in $C_{A,0}$ in the case of exothermic reactions brings about a rise in ΔT_{ad} , and the line runs at a lesser slope.

The fractional conversion x_A may also be increased by increasing the mean residence time $\bar{\tau} = V/v$. In all of the cases examined so far, the plot (see Figs. 10.3 through 10.6) representing the material balance will then be shifted to the left. With reversible reactions, there is a further constraint on the position of this plot — this constraint is the conditions of equilibrium, $x_{A,e}(T)$. Therefore, x_A can also be increased by changing the conditions affecting the equilibrium.

How the degree of conversion should be increased in each particular case should be decided on the basis of a careful analysis, including the relevant engineering and economic aspects.

The non-adiabatic well-stirred tank reactor under steady-state conditions. When analysing or designing a non-adiabatic well-stirred tank reactor, resort is made to the overall heat balance, Eq. (10.13):

$$vc_p \rho (T_0 - T) - \Delta H_r w_{rA} V \pm K_{ht} A_{ht} \Delta T_{ht} = 0$$

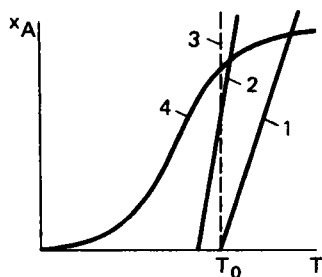


Fig. 10.7 Graphical solution of the material and heat balances over a perfectly mixed reactor effecting an irreversible exothermic reaction:

(1) heat balance over an adiabatic reactor; (2) same over a reactor with heat removal; (3) same over an isothermal reactor; (4) material balance

The driving force for heat transfer between the reaction mixture in the reactor and the surrounding heat transfer medium is ΔT_{ht} , or the mean difference in temperature between the reaction mixture and the surrounding medium. The temperature T of the reaction mixture is the same at any point in a perfectly mixed reaction vessel. If we assume that the mean temperature of the heat transfer medium is T_{im} , then

$$\Delta T_{ht} = |T_{im} - T|$$

Let us consider an exothermic reaction effected in a perfectly mixed reactor with heat transfer to the surroundings. Here $T > T_{im}$, and Eq. (10.13) may, in view of the material balance, be written as

$$vc_p\rho(T_0 - T) - \Delta H_r C_{A,0} x_A v - K_{ht} A (T - T_{im}) = 0 \quad (10.30)$$

The next step is to re-arrange Eq. (10.30) so that it has the form $x_A = x_A(T)$ and the material and heat balances can be solved graphically:

$$x_A = \frac{vc_p\rho T_0 + K_{ht} A T_{im}}{\Delta H_r C_{A,0} v} - \frac{vc_p\rho + K_{ht} A}{\Delta H_r C_{A,0} v} T \quad (10.31)$$

Equation (10.31) describes a straight line as does Eq. (10.20) which is the heat balance of an adiabatic well-stirred tank reactor, but it contains a greater free term and a greater slope term. Therefore, the line is shifted away from the line representing the heat balance of an adiabatic reactor and runs steeper (curve 2 in Fig. 10.7).

The same reasoning could be applied to reactors effecting endothermic reactions, that is, with heat input from a heat-transfer medium.

The extreme case of a non-adiabatic reactor is the isothermal reaction vessel in which all heat of reaction is balanced out by heat exchange with the surroundings. The heat balance of an isothermal reactor is represented by a straight line parallel to the axis of ordinates ($T = T_0$), curve 3 in Fig. 10.7.

10.3 The Non-Isothermal Batch Well-Stirred Tank Reactor

When writing a heat balance on a batch tank reactor over an arbitrary element of time, we may assume that

$$Q_{in} = Q_{out} = 0$$

On the other hand, a batch reactor effects processes which are unsteady state for basic reasons. Therefore, there will always be an accumulation of heat in such a reactor

$$Q_{acc} \neq 0$$

Therefore, the heat balance, Eq. (10.12), over a batch well-stirred tank reactor takes the form

$$-\Delta H_r w_{rA} V \pm K_{ht} A_{ht} \Delta T_{ht} = V[d(\rho c_p T)/d\tau] \quad (10.32)$$

Let us assume that the heat capacity and density of the reaction system are constant. Then,

$$-(\Delta H_r w_{rA} / \rho c_p) \pm (K_{ht} A_{ht} \Delta T_{ht} / V \rho c_p) = dT/d\tau \quad (10.33)$$

Equation (10.32) and the material balance

$$-w_{rA} V = d(V C_A)/d\tau \quad (10.34)$$

constitute between them a mathematical model of a non-isothermal batch reactor effecting homogeneous processes.

When simultaneously solved, Eqs. (10.33) and (10.34) define the form of the relation connecting temperature and concentration to residence time.

Example 10.1 A batch well-stirred tank reactor with a volume of $V = 1 \text{ m}^3$, enclosed in a cooling jacket (of surface area $A = 3 \text{ m}^2$) effects a 1st-order reaction



for which the rate equation has the form

$$w_{rA} = 2.5 \times 10^8 \exp(-50\,000/RT) C_A \text{ kmol m}^{-3} \text{ hr}^{-1}$$

The enthalpy change on reaction is $\Delta H_r = -165\,000 \text{ kJ kmol}^{-1}$. The reaction mixture has a constant density and a constant heat capacity, respectively equal to $\rho = 1110 \text{ kg m}^{-3}$ and $c_p = 3.4 \text{ kJ kg}^{-1} \text{ K}^{-1}$. The initial concentration of reactant A is $C_{A,0} = 2 \text{ kmol m}^{-3}$, and its initial temperature is $T_0 = 300\text{K}$. The overall heat-transfer coefficient $K_{ht} = 2500 \text{ kJ m}^{-2} \text{ hr}^{-1} \text{ K}^{-1}$. The temperature of the heat-transfer medium (coolant) is $T_c = 300\text{K}$.

Find how the fractional conversion and temperature change in the course of the reaction and compute the residence time to the instant when the fractional conversion is $x_A = 0.98$.

Solution. As usual, the degree of conversion will be characterized by the fractional conversion x_A .

Then the material and heat balances, Eq. (10.33) and Eq. (10.34), for the reactor in question will have the form

$$\left. \begin{aligned} C_{A,0} dx_A/d\tau &= w_{rA} = kC_{A,0}(1 - x_A) \\ -(\Delta H_r/\rho c_p)C_{A,0}(dx_A/d\tau) - (K_{ht}A/V\rho c_p)(T - T_c) &= dT/d\tau \end{aligned} \right\}$$

On substituting the numerical values, we get

$$\left. \begin{aligned} dx_A/d\tau &= 2.5 \times 10^8 \exp(-50000/RT)(1 - x_A) \\ dT/d\tau &= \frac{1.7 \times 10^5 \times 2}{1110 \times 3.4} (dx_A/d\tau) - \frac{2500 \times 3}{1110 \times 3.4 \times 1} (T - 300) \end{aligned} \right\}$$

or

$$\left. \begin{aligned} dx_A/d\tau &= (1 - x_A) \exp(19.32 - 5995/T) \\ dT/d\tau &= 90(dx_A/d\tau) - 2(T - 300) \end{aligned} \right\}$$

For a numerical solution of the above system of equations, we replace the differentials with finite changes:

$$\left. \begin{aligned} \Delta x_A &= \Delta\tau(1 - x_A) \exp(19.32 - 5995/T) \\ \Delta T &= 90\Delta x_A - 2(T - 300)\Delta\tau \end{aligned} \right\}$$

It is convenient to do computations by the iteration method. Assume that $\Delta\tau = 0.1$ hr. As a zero approximation, we take $\Delta x_A = 0.1$ and $\Delta T = 10$ K. We take it that the initial values are chosen correctly if the computed value of Δx_A differs from the specified one by not more than 0.001 and the computed temperature differs from the given one by not more than 0.3K. Thus, the difference in each case will be about 0.1% of the absolute value.

If $\Delta x_A = 0.1$, then the mean value of x_A over the specified interval of integration will be

$$\bar{x}_A = 0.1/2 = 0.05$$

and the mean temperature in the reactor over the same time interval $\Delta\tau$ will be

$$\bar{T} = T_0 + \Delta T/2 = 300 + 10/2 = 305\text{K}$$

On substituting the above values in the system of equations, we get

$$\begin{aligned} \Delta x_A &= 0.1(1 - 0.05) \exp(19.32 - 5995/305) = 0.068 \\ \Delta T &= 90 \times 0.1 - 2(305 - 300) \times 0.1 = 8 \end{aligned}$$

Since the difference between the computed and specified values of Δx_A and ΔT exceeds the limit of error, we carry out a second iteration step, on assuming that the initial values are $\Delta x_A = 0.068$ and $\Delta T = 8\text{K}$:

$$\begin{aligned}\bar{x}_A &= 0.068/2 = 0.034 \text{ and } \bar{T} = 304\text{K} \\ \Delta x_A &= 0.1(1 - 0.034) \exp(19.32 - 5995/304) = 0.065 \\ \Delta T &= 90 \times 0.068 - 2(304 - 300) \times 0.1 = 5.3\end{aligned}$$

The third iteration step gives

$$\begin{aligned}\bar{x}_A &= 0.065/2 = 0.0325 \text{ and } \bar{T} = 302.65\text{K} \\ \Delta x_A &= 0.1(1 - 0.0325) \exp(19.32 - 5995/302.65) = 0.0594 \\ \Delta T &= 90 \times 0.065 - 2(302.65 - 300) \times 0.1 = 5.3\text{K}\end{aligned}$$

The fourth iteration step gives

$$\begin{aligned}\bar{x}_A &= 0.059/2 = 0.0295 \text{ and } \bar{T} = 302.65\text{K} \\ \Delta x_A &= 0.1(1 - 0.0295) \exp(19.32 - 5995/302.65) = 0.0595 \\ \Delta T &= 90 \times 0.059 - 2(302.65 - 300) \times 0.1 = 4.8\text{K}\end{aligned}$$

Finally, over the time interval from $\tau_0 = 0$ to $\tau_1 = 0 + \Delta\tau = 0.1$ hr, we take

$$\begin{aligned}\Delta x_A &= 0.059 \text{ and } x_A = 0 + 0.059 = 0.059 \\ \Delta T &= 4.8\text{K and } T = 300 + 4.8 = 304.8\text{K}\end{aligned}$$

Proceeding in a similar way, we then do the computations for the time interval from $\tau_1 = 0.1$ hr to $\tau_2 = 0.2$ hr, etc.

The computer-generated results are given in Table 10.1 and plotted in Fig. 10.8.

On the basis of the above results we conclude that the time required to achieve $x_A = 0.98$ is 1.1 hr, and the final temperature of the reaction mixture is

$$T = 300 + 27.51 = \text{approx } 328\text{K}$$

Table 10.1 Computational Results for a Non-Isothermal Batch Well-Stirred Tank Reactor

τ	Δx_A	ΔT	x_A	$T - T_0$	τ	Δx_A	ΔT	x_A	$T - T_0$
0	—	—	0.000	0.00	0.7	0.148	4.64	0.845	45.80
0.1	0.059	4.80	0.059	4.80	0.8	0.080	-1.79	0.925	44.00
0.2	0.076	5.31	0.134	10.10	0.9	0.034	-5.23	0.959	38.77
0.3	0.098	6.15	0.232	16.21	1.0	0.015	-5.87	0.973	32.90
0.4	0.126	7.37	0.358	23.62	1.1	0.007	-5.39	0.981	27.51
0.5	0.160	8.76	0.518	32.38	1.2	0.004	-4.66	0.885	22.85
0.6	0.179	8.78	0.697	41.16					

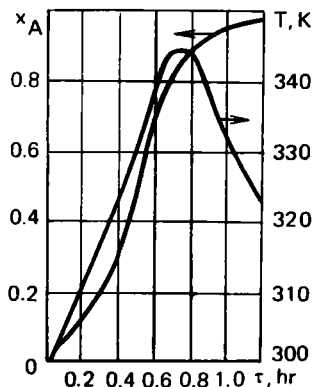


Fig. 10.8 To Example 10.1

For an adiabatic batch reactor, the heat balance, Eq. (10.33), takes a simpler form:

$$dT/d\tau = -(\Delta H_r/\rho c_p)w_{rA} \quad (10.35)$$

We assume, as we did in the previous cases, that the ratio $\Delta H_r/\rho c_p$ is independent of temperature. On substituting

$$w_{rA} = C_{A,0}(dx_A/d\tau)$$

for w_{rA} in Eq. (10.35), we get

$$dT/d\tau = (C_{A,0}\Delta H_r/\rho c_p)(dx_A/d\tau) = \Delta T_{ad}(dx_A/d\tau) \quad (10.36)$$

On integrating, we have

$$T - T_0 = \Delta T_{ad}x_A \quad (10.37)$$

or

$$x_A = (1/\Delta T_{ad})(T - T_0) \quad (10.38)$$

That is, in an adiabatic batch well-stirred tank reactor the change of temperature is directly proportional to the change in conversion, as it is in a continuous flow reactor under steady-state conditions.

The mathematical model of an adiabatic batch well-stirred tank reactor will include Eq. (10.36) and the material balance

$$-w_{rA}(C_A)V = d(C_A V)/d\tau$$

or

$$C_{A,0}(dx_A/d\tau) = w_{rA}(x_A) = k_0 \exp(-E/RT)f(x_A) \quad (10.39)$$

On substituting the temperature computed from the heat balance (10.37) in Eq. (10.39), we obtain the following expression for an irreversible reaction of an arbitrary order:

$$C_{A,0}(dx_A/d\tau) = k_0 \exp[-E/R(T_0 + \Delta T_{ad}x_A)]f(x_A) \quad (10.40)$$

where $f(x_A)$ is the functional relation connecting the reaction rate to the conversion of species A.

On integrating the above equation, we get

$$\tau = C_{A,0} \int_0^{x_A} \frac{dx_A}{k_0 \exp \left[-\frac{E}{R(T_0 + \Delta T_{ad} x_A)} \right] f(x_A)} \quad (10.41)$$

As a rule, the integration has to be done by numerical methods. Equation (10.41) offers a tool for the analysis and design of adiabatic batch-type perfectly mixed (well-stirred) reactors.

10.4 The Non-Isothermal Ideal (Plug Flow) Tubular Reactor

As with other balances, the heat balance for a plug flow tubular reactor is written over an infinitesimal volume $dV = A dz$ because in the general case the temperature distribution along the reactor axis is other than uniform. If we take a reactor in the form of a cylindrical conduit of a constant cross-sectional area $A = \pi R^2$ (where R is the radius of the cylindrical conduit) in which a constant-composition feedstock is moving at a constant linear velocity u , the heat balance over an element of volume will have the form

$$\begin{aligned} u c_p \rho T d\tau - u c_p \rho \left(T + \frac{\partial T}{\partial z} dz \right) d\tau - w_{rA} A dz \Delta H_r d\tau \\ \pm K_{ht} dA_{ht} \Delta T_{ht} d\tau = c_p \rho V (\partial T / \partial \tau) d\tau \end{aligned} \quad (10.42)$$

where dA_{ht} is the infinitesimal area through which the volume element exchanges heat with the surroundings. If heat transfer is through the reactor wall, then

$$dA_{ht} = 2\pi R dz$$

After simple manipulations, we obtain for steady-state conditions

$$-u(dT/dz) - w_{rA}(\Delta H_r/c_p \rho) \pm 2K_{ht}\Delta T_{ht}/Rc_p \rho = 0 \quad (10.43)$$

The heat balance, Eq. (10.43), must be solved simultaneously with the material balance

$$-u(dC_A/dz) - w_{rA}(C_A) = 0 \quad (10.44)$$

which may be re-cast as

$$uC_{A,0}(dx_A/dz) - k_0 \exp(-E/RT)f(x_A) = 0 \quad (10.45)$$

By solving Eqs. (10.43) and (10.45), we can obtain the distribution of the fractional conversion and temperature along the reactor, that is, determine the form of the relations $T(z)$ and $x_A(z)$ or $T(x_A)$ for a plug flow tubular reactor under steady-state conditions.

For an adiabatic plug flow tubular reactor, Eq. (10.43) takes the form

$$-u(dT/dz) - w_{rA}(\Delta H_r/c_p\rho) = 0 \quad (10.46)$$

On substituting in Eq. (10.46) for w_{rA} as expressed with the aid of the material balance, Eq. (10.44),

$$w_{rA} = -u(dC_A/dz) = uC_{A,0}(dx_A/dz) \quad (10.47)$$

we obtain

$$-u(dT/dz) - uC_{A,0}(dx_A/dz)(\Delta H_r/c_p\rho) = 0$$

or, on eliminating dz ,

$$dT/dx_A = -C_{A,0}\Delta H_r/c_p\rho \quad (10.48)$$

If we assume that over the specified time interval ΔH_r , c_p and ρ are constant, then the integration of Eq. (10.48) will yield a linear relationship between changes in temperature and conversion in an adiabatic plug-flow tubular reactor

$$T - T_0 = -(\Delta H_r C_{A,0}/c_p\rho)x_A = -\Delta T_{ad}x_A \quad (10.49)$$

which checks with the respective relations for batch and continuous flow stirred-tank reactors.

Using Eq. (10.49), we may write the mathematical model for an adiabatic plug flow tubular reactor effecting irreversible, homogeneous n th-order reactions as a single equation of the form

$$C_{A,0}u(dx_A/dz) - k_0 \exp[-E/R(T_0 - \Delta T_{ad}x_A)]f(x_A) = 0 \quad (10.50)$$

or

$$\bar{\tau} = zA/uA = V/v = C_{A,0} \int_0^{x_A} \frac{dx_A}{k_0 \exp[-E/R(T_0 - \Delta T_{ad}x_A)]f(x_A)} \quad (10.51)$$

10.5 Thermal Stability of Chemical Reactors

As has been noted earlier, the system of material and heat balances over an adiabatic well-stirred tank reactor effecting exothermic reactions may have several solutions. For example, when curve 2 intersects curve 4 in Fig. 10.4 (a 1st-order irreversible exothermic reaction), the system of material and heat balances has three solutions respectively corresponding to points *B*, *C* and *D*. The graphically solvable system of equations was written on the assumption that the reactor was operating under steady-state conditions, that is, with the process variables (notably, temperature and

fractional conversion) remaining constant with time. It may be argued that the several solutions imply the possibility of several steady states.

Of course, only one of the three likely solutions would be realized in practice. It is desirable that the reactor be operated so that the conversion of the reactant could be as high as possible, that is, could correspond to point *D*. Is this feasible? How can we secure the most advantageous of the likely steady states in practice? Answers to these questions can be deduced by analysing the available steady states for stability.

The stability of a system under steady-state conditions can be assessed from the system's response to a stimulus.

A system is said to be in a stable steady state if a small instantaneous stimulus, or disturbance, cannot drive the system beyond the small region surrounding the steady state in question.

If we disturb a system residing in a stable steady state and then leave it to itself, it will recover its previous steady state of its own accord. In contrast, if we disturb a system residing in an unstable steady state it will, upon removal of the disturbance, move to another, stable state.

Before going any further in our analysis of the thermal stability of chemical reactors under steady-state conditions, let us turn to a mechanical analogy — the travel of a ball over various surfaces. In the case shown in Fig. 10.9*a*, the ball will find itself in a steady state of rest at the bottom of the “bowl”. When the shape is as shown in Fig. 10.10*a*, chances are that the ball will move over the saddle beyond the origin of coordinates. At the origin of coordinates (see Fig. 10.10) the ball may be said to be in an unstable steady state (this state is feasible, but the slightest push will disturb the ball from this equilibrium state).

Basically, the differences between the stable steady state at the bottom of the “bowl” and the unstable steady state in the saddle may be illustrated by projections of the ball's travel paths onto the (*x*, *y*)-plane. The plane is called the *phase plane* and the projections are referred to as *phase trajectories*. The shape of the phase trajectories becomes especially instructive

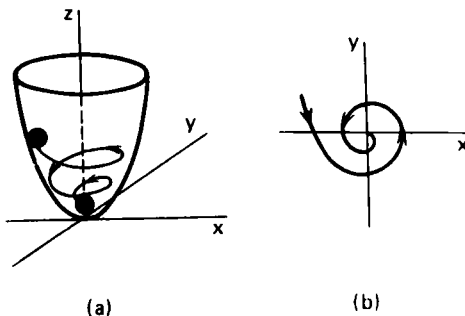


Fig. 10.9 (a) A “bowl” in three dimensions and (b) projections of a ball's travel paths onto a plane

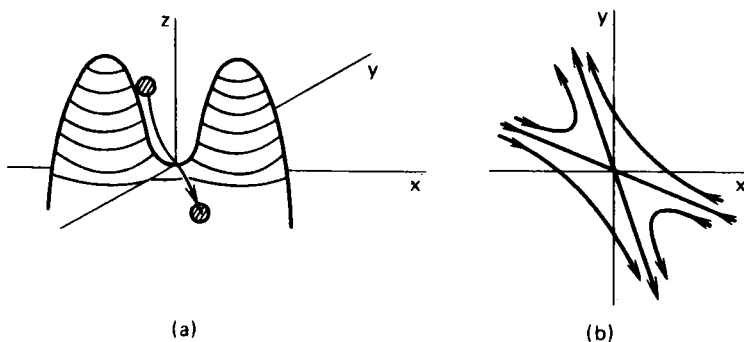


Fig. 10.10 (a) A “saddle” in three dimensions and (b) projections of a ball’s travel paths on a plane

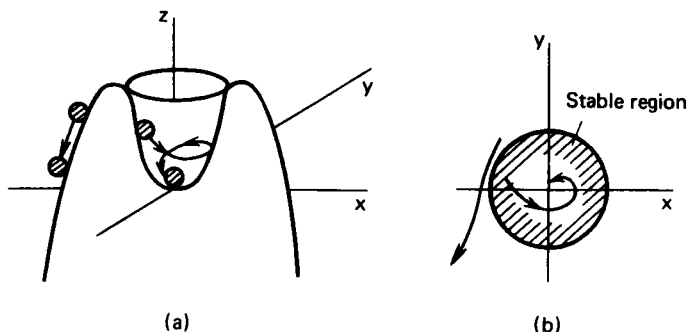


Fig. 10.11 (a) A “volcano’s crater” in three dimensions and (b) projections of a ball’s travel paths on a plane

when the ball is moving over symmetrical surfaces. Figures 10.9b and 10.10b show the travel paths of a ball in two distinct cases, one in which a stable steady state is feasible, and the other in which only an unstable steady state is possible. For simplicity, the figures do not show oscillations of the ball.

A stable steady state is *feasible* when the stable region at the bottom of the bowl is limited in size, as should be in practical problems. Then the surface over which the ball travels becomes similar to that of a volcano’s crater (Fig. 10.11a). One of the trajectories will then enclose on the (x, y) -plane a limited stable region inside which all trajectories terminate in a stable steady state (Fig. 10.11b). The trajectories outside this region diverge away from the stable region.

As a first step in our analysis of the three steady states at points B , C and D for stability in the case of an adiabatic well-stirred tank reactor (see Fig. 10.4), we will consider the physical aspects of the process taking place in the reactor. To this end, we re-arrange Eqs. (10.20) and (10.24) on multiplying them by the enthalpy change on reaction, ΔH_r .

The heat balance, Eq. (10.20), takes the form

$$x_A \Delta H_r = q_- = (c_p \rho / C_{A,0}) T_0 - (c_p \rho / C_{A,0}) T \quad (10.52)$$

The ratio between the product of the heat capacity by the density of the reaction mixture by its temperature, on the one hand, and the initial concentration is the sensible heat of the reaction mixture per kilomole of reactant entering the reactor. In the case of an exothermic reaction, $T_0 < T$; the term q_- in Eq. (10.52) shows by how much the sensible heat removed from the reactor with the exit stream exceeds the sensible heat supplied to the reactor by the feed stream. Since q_- is a quantity per kilomole of reactant A , it may be called the *specific heat removal* from the reactor.

Equation (10.24) shows how much the fractional conversion of the reactant is increased due to the chemical process effected in the reactor. If we multiply this quantity by the enthalpy change on exothermic reaction, ΔH_r , as measured in the kJ kmol^{-1} of reactant A entering the reactor, we will obtain q_+ , or the *specific heat release* in the reactor, per kilomole of reactant A entering the reactor.

Since we have assumed that ΔH_r is constant, multiplying Eqs. (10.20) and (10.24) by it can only change the scale of the plot used to solve the equations of material and heat balances numerically. Now the intersections of the lines in the plot of Fig. 10.5 acquire a different physical meaning. At these points the specific heat removal is equal to the specific heat release — a condition assuring a stable steady state. Should this equality be upset by, say, an instantaneous disturbance in the inlet stream, either q_+ or q_- will predominate and, in consequence, the temperature in the reaction vessel will rise or fall of its own accord.

Let us examine in more detail the steady states when the system of material and heat balances has more than one solution.

Figure 10.12a shows a q -vs- T diagram onto which the upper intersection point D is transferred from Fig. 10.4. Suppose that the thermal equilibrium of the system has been upset by some disturbance, such as an increase in the system's temperature, T_{D+} . In this condition, the specific heat removal q_- exceeds the specific heat release, but, after the disturbance is removed, the temperature will fall of its own accord to T_D . In other words, the system will recover its previous state of equilibrium. If the system be disturbed so that its temperature falls to T_{D-} , it will spontaneously rise to T_D upon removal of the disturbance because q_+ exceeds q_- . Thus, point D represents a stable steady state for an adiabatic perfectly mixed reactor.

On analysing the thermal equilibrium at point B (Fig. 10.12b) we may likewise conclude that this solution of the system of balance equations corresponds to a stable steady state.

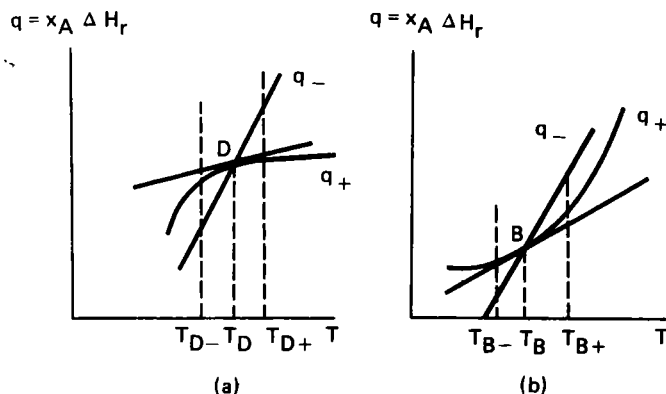


Fig. 10.12 Stable steady states of an adiabatic perfectly mixed reactor effecting an exothermic reaction

The situation will be different at the middle point of intersection, *C* (Fig. 10.13). A departure from equilibrium to the right along the temperature axis will lead to a further spontaneous rise in temperature, while a departure to the left will lead to a further spontaneous fall in temperature. Thus, at point *C* the system is in a state of unstable equilibrium.

It should be noted that in stable steady states the derivative dq_+/dT , or the slope of the tangent to the $q_+(T)$ curve at the points of intersection, is smaller than the slope of the tangent to the $q_-(T)$ curve:

$$dq_+/dT < |c_p \rho / C_{A,0} \Delta H_r| \quad (10.53)$$

On the contrary, in unstable states

$$dq_+/dT > |c_p \rho / C_{A,0} \Delta H_r| \quad (10.54)$$

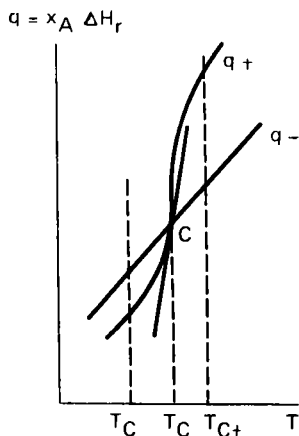


Fig. 10.13 An unstable steady state of an adiabatic perfectly mixed reactor effecting an exothermic reaction

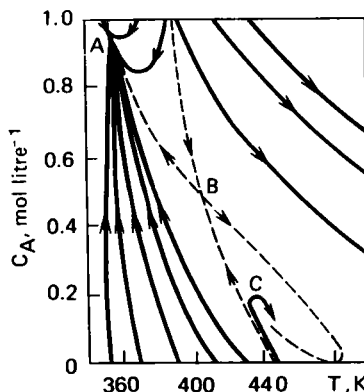


Fig. 10.14 Phase plane showing a multiplicity of steady states for a continuous flow stirred reactor

The above inequalities may be used to analyse reactors for stability.

The need to analyse a system's steady states for stability arises from the fact that one has to reckon with unavoidable transients (short-duration departures from thermal equilibrium and, as a consequence, short-duration transients in the process variables with time). The unsteady-state material and heat balances over a continuous flow well-stirred tank reactor may be written as

$$\left. \begin{aligned} dC_A/d\tau &= f_1(C_A, T) \\ dT/d\tau &= f_2(C_A, T) \end{aligned} \right\} \quad (10.55)$$

Systems of differential equations like Eqs. (10.55) lend themselves to a graphical analysis in which the dependent variables C_A and T are regarded as coordinates on a phase plane. Using equations like (10.55), each state of a system can be located as a point on the (C_A, T) phase plane for any fixed values of various parameters.

Since an unsteady-state system passes with time through a series of states, starting with the initial one and ending up with the final one, their representation on the (C_A, T) plane produces phase trajectories. In outward appearance, these phase trajectories resemble the travel paths of a ball moving over various surfaces (see Figs. 10.9 through 10.11). For example, Fig. 10.14 shows a phase plane with three steady states for a continuous flow stirred tank reactor. In this figure, points *A* and *C* represent stable steady states (the phase trajectories converge on a node or they converge to a focus on spiral paths), while point *B* represents an unstable steady state (the trajectories diverge on the saddle surface).

Thus, by analysing steady states for stability, the designer can predict which set of operating conditions of an adiabatic reactor effecting an exothermic reaction is to be avoided as failing to assure the desired thermal stability of the process. For example a minor disturbance at the inlet to the

reactor operating under conditions represented by point *C* in Fig. 10.4 would cause the reactor to move spontaneously to point *D* or point *B*. In the last mentioned case, the reactor would give only a very low degree of conversion — obviously, this condition is unattractive from a practical point of view.

Therefore, when choosing process conditions for exothermic reactions, it is usually sought to maintain an only stable state giving a high degree of conversion. This could be done by varying the initial temperature T_0 so that the plot representing the heat balance is shifted to the right, or by varying the mean residence time $\bar{\tau}$ so that the curve representing the material balance is shifted to the left. Unfortunately, either solution may be unattractive economically. If, in such cases, the reactor is to reach the upper point *D* (see Fig. 10.4) of its own accord, the temperature at start-up must exceed the temperature corresponding to the unstable steady state represented by point *C*.

10.6 Optimum Operating Temperatures in Industrial Reactors

In the preceding sections we have examined various thermal conditions in which chemical reactors may operate and also how the manner of heat transfer can be accounted for in mathematical models.

Optimum operating temperatures are those at which the chemical process in question proceeds so that the reactor shows an economically justifiable maximum throughput per unit volume of the reactor in terms of the desired product (an economically justifiable maximum production rate).

More than one approach may be used to define optimum operating temperatures, the choice being dependent on the type of chemical reaction involved. Obviously, a given reactor can attain a maximum production rate when the process it is effecting proceeds likewise at a maximum attainable rate. Therefore, it is worth while examining how the type of rate equation affects the choice of operating temperatures.

Simple irreversible reactions. The rate equation for irreversible exothermic and endothermic reactions may be written generally as

$$w_{rA} = k_0 \exp(-E/RT)f(x_A) \quad (10.56)$$

and, for a 1st-order reaction, as

$$w_{rA} = k_0 \exp(-E/RT)C_{A,0}(1 - x_A) \quad (10.57)$$

The rate of reaction is a function of several variables, notably temperature and fractional conversion (or reactant concentration). As follows from Arrhenius's equation, the rate constant monotonically in-

creases with increasing temperature. It is seen from Eqs. (10.56) and (10.57) that there is nothing of fundamental nature that could prevent one from speeding up an irreversible reaction through a rise in temperature. A rise in the fractional conversion, however, brings about a fall in the rate of reaction. This could be compensated for by raising the temperature of the process.

Endothermic reactions are accompanied by absorption of heat. Therefore, it is not attractive to effect such reactions adiabatically because as a reaction progresses, its rate will fall off both due to an increase in the fractional conversion and due to a decrease in the temperature. It is more reasonable to effect endothermic processes in reactors with heat input from without (isothermal or heat-regulated reactors) while maintaining their temperature at a value maximally allowable from structural considerations, that is, one which can be tolerated by the materials of construction. This, however, calls for a further economic analysis to weigh the likely increase in profit due to a higher output from the reactor against the increased cost of maintaining the higher temperature.

With irreversible exothermic reactions, a rise in conversion is accompanied by release of heat. Therefore, when the process is effected adiabatically, this would raise the temperature of the reaction mixture. The decrease in the rate of reaction due to the increase in conversion will partly be offset by the increase in the rate constant with increasing temperature. By effecting such a reaction in an adiabatic continuous reactor, it is possible to obtain a high reaction rate and a high reactor output without resort to heat input from external sources. The heat of the reaction mixture leaving the reactor can then serve to raise the inlet temperature of the reactants.

Reversible chemical reactions. An example of a simple 1st-order reversible reaction is $A \rightleftharpoons R$. Its rate is given by

$$w_{rA} = k_1 C_A - k_2 C_R = k_{10} \exp(-E_1/RT) C_A - k_{20} \exp(-E_2/RT) C_R \quad (10.58)$$

or, see Eq. (10.28),

$$w_{rA} = k_1 C_{A,0} (1 - x_A/x_{A,e}) \quad (10.59)$$

On the one hand, similarly to the rate of the irreversible reaction (10.57), it is a function of the rate constant k_1 and the fractional conversion x_A . On the other hand, it is decided by how closely the reactive system comes to a state of chemical equilibrium and by the maximally attainable equilibrium conversion $x_{A,e}$.

The manner in which the reaction rate changes with increasing temperature is different for endothermic and exothermic reactions.

An increase in the temperature at which a reversible endothermic reaction is effected brings about a rise in both the rate constant k_1 and the

equilibrium fractional conversion $x_{A,e}$. Therefore, when x_A is held at a constant value, the rate of a reversible endothermic reaction will increase monotonically with increasing temperature. Also, the choice of optimum operating temperatures for such reactions will be similar to that for irreversible endothermic reactions.

The situation is different with reversible exothermic reactions. Since the rate of reaction is a function of several variables (at least, two — T and x_A), this function can conveniently be analyzed by using its section where all variables, except one, are maintained at constant values.

This approach simplifies the graphical presentation of the function. A function of n variables, $f(x_1, x_2, \dots, x_n)$, is graphically depicted as a surface in an $(n + 1)$ -dimensional space. A section of the function may be visualized as a family of $f(x_1, x_2, \dots, x_n) - x_i$ curves in a plane, with the variables $x_1, x_2, \dots, x_{i-1}, x_{i+1}, x_n$ held constant.

Let us consider two forms of section of the function $w_{rA}(x_A, T)$: one with x_A held constant, and the other with T held constant.

We choose the fractional conversion such that $0 < x_{A,1} < 1$. For this degree of conversion, the reactant concentration in the reaction $A \rightleftharpoons R$ will be

$$C_{A,1} = C_{A,0}(1 - x_{A,1})$$

and the product concentration will be

$$C_{R,1} = C_{A,0}x_{A,1}$$

As the temperature rises, the rate constant of the forward reaction increases or, which is the same, the factor $k_1 C_{A,0}$ in Eq. (10.59) increases. At the same time, however, the equilibrium conversion $x_{A,e}$ decreases and, since $x_{A,1}$ is constant, the system moves closer to a state of equilibrium or, which is the same, the second factor in Eq. (10.59) decreases. Thus, we have two opposing effects that occur at the same time. At low temperatures when the rate of rise in the ratio $x_{A,1}/x_{A,e}$ is lower than the rate of rise in k_1 with increasing temperature, the first (increasing) factor is stronger in its effect. At some temperature T_{1e} the chosen conversion $x_{A,1}$ becomes equal to the equilibrium conversion and the rate of reaction falls to zero. When this temperature is approached from the left, the second factor showing how close the system is to equilibrium is stronger in its effect. Obviously, there is some optimum temperature T_{1m} at which the reaction rate is a maximum at the specified degree of conversion. Let us find this temperature, using techniques of mathematical analysis (the search for the extremum of a function). For this purpose we differentiate the function defined in (10.58) with respect to temperature, assuming that C_A and C_R are constant, and equate the derivative to zero:

$$\begin{aligned} (\partial w_{rA} / \partial T)_{C_A, C_R} &= C_A k_{10} (E_1 / RT^2) \exp(-E_1 / RT) \\ &\quad - C_R k_{20} (E_2 / RT^2) \exp(-E_2 / RT) \end{aligned} \quad (10.60)$$

Hence, at $T = T_m$,

$$(E_2 - E_1)/RT_m = \ln (k_{20}C_R E_2/k_{10}C_A E_1)$$

or

$$\begin{aligned} T_m &= \frac{E_2 - E_1}{R \ln (k_{20}C_R E_2/k_{10}C_A E_1)} \\ &= \frac{E_2 - E_1}{R \ln [k_{20}E_2x_A/k_{10}E_1(1 - x_A)]} \end{aligned} \quad (10.61)$$

Equation (10.61)* gives the optimum temperature for any fractional conversion, except $x_A = 0$ and $x_A = 1$ when the function $w_{rA}(T, x_A)$ has no maximum.

Now we can construct a section of the function $w_{rA}(T, x_A)_{x_A=x_{A,1}}$ (curve 1 in Fig. 10.15). For another fractional conversion, $x_{A,2} > x_{A,1}$, the plot of the function $w_{rA}(T, x_A)_{x_A=x_{A,2}}$ is likewise depicted by a curve with a peak. It intersects the axis of abscissas at point T_{2e} which lies to the left of point T_{1e} because reversible exothermic reactions result in a greater equilibrium conversion at a lower temperature or, which is the same, $x_{A,2}$ becomes equal to $x_{A,e}$ at a lower temperature. It follows from Eq. (10.61) that an increase in the fractional conversion is accompanied by a decrease in the optimum temperature, T_{2m} , because the function $y = x_A/(1 - x_A)$ in the denominator of the equation is an increasing one. Thus the plot of $w_{rA}(T)_{x_A=x_{A,2}}$ (curve 2 in Fig. 10.15) runs lower than the plot of $w_{rA}(T)_{x_A=x_{A,1}}$ (curve 1 in Fig. 10.15), and its peak is shifted to the left.

Figure 10.16 is a plot of the reaction rate for the catalytic oxidation of sulphur dioxide as a function of temperature for different fractional conversions of SO_2 . On joining the peaks on the sections of $w_{rA}(T)$, we obtain an optimum temperature sequence or profile.**

When a process is effected in accord with an optimum temperature sequence, the temperature in the reactor should be brought down as the degree of conversion increases — this is necessary for the rate of reaction to remain always as near its maximum value as practicable.

That the rate of reaction cannot be higher than it is when a process is effected in accord with an optimum temperature sequence can be proved as follows. Consider sections of the function $w_{rA}(T, x_A)$ at several values of temperature, that is, the relation between the rate of reaction and fractional conversion.

* The same result could have been obtained from Eq. (10.59) but this would have involved a good deal of unwieldy mathematics.

** See A.R. Cooper and G.V. Jeffreys, *Chemical Kinetics and Reactor Design*. — *Translator's note*.

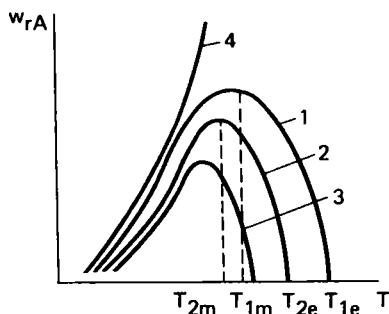


Fig. 10.15 Section of the function $w_{rA} = w_{rA}(x_A, T)$ at a given fractional conversion:

1, $x_{A,1}$; 2, $x_{A,2}$; 3, $x_{A,3}$
 $(x_{A,1} < x_{A,2} < x_{A,3})$; 4, $x_A = 0$

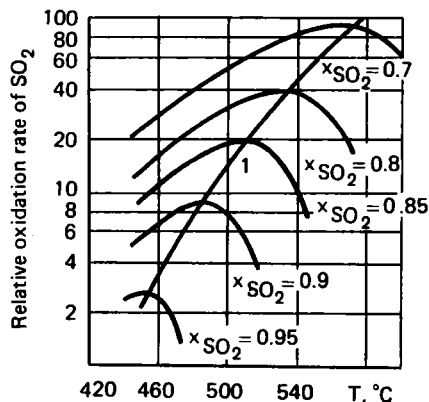


Fig. 10.16 Rate of oxidation of SO_2 over a vanadium catalyst as a function of temperature for several fractional conversions:

1, line of optimum operating temperatures

When $T = T_1 = \text{const}$, then k_1 and $x_{A,e}$, which are temperature-dependent and enter Eq. (10.59), are likewise constant. Then Eq. (10.59) describes a straight line which intersects the axis of abscissas at point $x_A = x_{A,e}$, and the axis of ordinates at point $w_{rA} = k_1(T_1)C_{A,0}$ (line 1 in Fig. 10.17). At another temperature, $T_2 > T_1$, the intersection between the line and the axis of abscissas moves to the left, and the intersection between the line and the axis of ordinates moves upwards. Figure 10.17 shows a family of sections such that $T_1 < T_2 < T_3 < T_4 < \dots < T_n$. In this case, the optimum temperature sequence is the envelope of the family of lines. It is seen from Fig. 10.17 that at no temperature may the rate of reaction be higher than the values bounded by the optimum temperature profile.

In practical applications, the optimum temperature profile is often plotted on the $x_A - T$ coordinates, in which case the abscissas of points on the profile are the temperatures assuring a maximum rate of reaction for the conversions which are the ordinates of the same points. This profile may be plotted, using an equation of form (10.61). Figure 10.18 shows the optimum temperature profile for the oxidation of sulphur dioxide over a vanadium (V_2O_5) catalyst, the composition of the gaseous feedstock being SO_2 , 7% by volume and O_2 , 11% by volume. In this plot, curves 2 correspond to the case when the rate of reaction is 80% of the maximum value.

As already noted, when a process is effected along the optimum temperature profile, the reactor is operating at a maximum production rate (output per unit volume or unit mass). As an example, let us compare two cases each involving a 1st-order reversible exothermic reaction effected in a

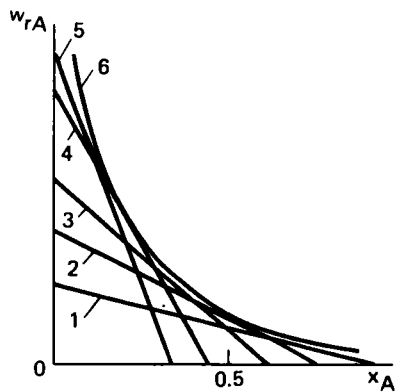


Fig. 10.17 Sections of the function $w_{rA} = w_{rA}(x_A, T)$ at constant temperatures: 1, T_1 ; 2, T_2 ; 3, T_3 ; 4, T_4 ; 5, T_5 ($T_1 < T_2 < T_3 < T_4 < T_5$); 6, line of optimum operating temperatures

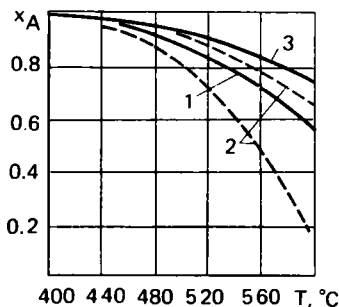


Fig. 10.18 Oxidation of SO_2 over a vanadium catalyst: 1, line of optimum operating temperatures; $w_{rA} = w_{rA,opt}$; 2, $w_{rA} = 0.8 w_{rA,opt}$; 3, equilibrium

plug flow reactor. In case (1) the temperature is maintained at a constant value assuring the highest attainable fractional conversion. In case (2) the temperature is varied to follow the optimum temperature profile.

Example 10.2 A 1st-order reversible exothermic reaction



is effected in a plug flow tubular reactor. The mean residence time, $\bar{\tau} = V/v$, is 1 hr. The reaction variables are as follows.

Enthalpy change on reaction $\Delta H_r = -70 \text{ MJ kmol}^{-1}$

Equilibrium constant at 298 K $K_{298} = 20$

Rate constant for the forward reaction $k_1 = 5 \times 10^8 \exp(-50000/RT) \text{ hr}^{-1}$

The reaction can be effected (1) with the reactor temperature held constant and (2) with the reactor temperature varied in accord with the optimum temperature profile. It is required to find:

(1) The optimum temperature that will assure the highest fractional conversion in case (1) and the respective mean residence time $\bar{\tau}$.

(2) The optimum mean residence time, $\bar{\tau}_{opt}$, with the reaction effected along the optimum temperature profile until the fractional conversion is the same as that achieved at constant temperature.

Solution. If the reaction is effected at constant temperature, we need only the material balance over the reactor to describe it. For a plug flow

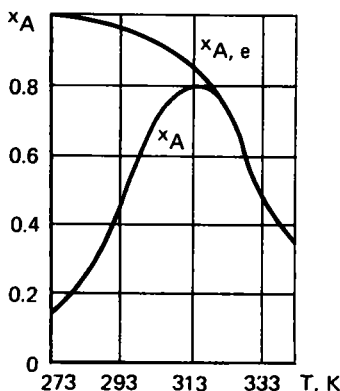


Fig. 10.19 To Example 10.2

tubular reactor, the material balance takes the form

$$\begin{aligned}\bar{\tau} &= C_{A,0} \int_0^{x_A} dx_A / w_{rA}(x_A) = C_{A,0} \int_0^{x_A} dx_A / [k_1 C_{A,0} (1 - x_A/x_{A,e})] \\ &= -(1/k_1) x_{A,e} \ln (1 - x_A/x_{A,e})\end{aligned}$$

Hence,

$$x_A = x_{A,e} [1 - \exp (1 - k_1 \bar{\tau} / x_{A,e})] \quad (10.62)$$

On substituting $k_1 = k_1(T)$ and $x_{A,e} = x_{A,e}(T)$ into Eq. (10.62), we get the relation connecting the fractional conversion x_A to temperature. On equating the derivative dx_A/dT to zero, we can determine the optimum temperature and the respective fractional conversion. The equation that results from differentiation is a transcendental one in temperature, and it must be solved by numerical methods. The optimum temperature can be found differently, on finding x_A by Eq. (10.62) for several values of temperature and constructing an $x_A(T)$ plot.

The data required to construct this plot are given in Table 10.2, and the results are presented in Fig. 10.19. The equilibrium fractional conversion $x_{A,e}$ is found by the equation

$$x_{A,e} = K/(1 + K)$$

where K is the equilibrium constant found by the van't Hoff equation

$$d \ln K / dt = \Delta H_r / RT^2$$

Hence,

$$\ln K_1 / K_{298} = -(\Delta H_r / R)(1/T - 1/298)$$

Thus, it is seen that the optimum temperature is 316 K, and the maximum fractional conversion achieved is $x_{A,m} = 0.80$, if $\bar{\tau} = 1$ hr.

Table 10.2 Fractional Conversion in an Isothermal Reactor

Temp., K	Equilibrium constant, K	Equilibrium conversion, $x_{A,e}$	Rate constant for forward reaction, k_1 , hr^{-1}	x_A
273	263	0.996	0.145	0.135
283	89.0	0.989	0.316	0.270
293	32.3	0.970	0.650	0.474
303	12.6	0.926	1.478	0.693
313	5.19	0.838	2.404	0.791
323	2.26	0.693	4.350	0.692
333	1.04	0.509	7.596	0.509
343	0.50	0.332	12.8	0.332

Now we will find $\bar{\tau}_{opt}$ for the same reaction effected along the optimum temperature profile. For this purpose, we substitute the reaction rate as a function of the conversion corresponding to the optimum temperature in the material balance. This function is difficult to deduce analytically, but it can readily be obtained graphically by constructing sections of $w_{rA}(x_A)_T$, similar to those in Fig. 10.17.

The data required for the construction can be found in Table 10.2 (the intersections of the straight lines and the axis of abscissas give $x_{A,e}$, and the intersections of the same lines with the axis of ordinates give $k_1 C_{A,0} = k_1 \times 1 = k_1$). The plot of $w_{rA}(x_A)$ corresponding to the optimum temperature profile is presented in Fig. 10.20 (line 1). Since the function $w_{rA}(x_A)$ is now specified by a plot and not by an equation, the material

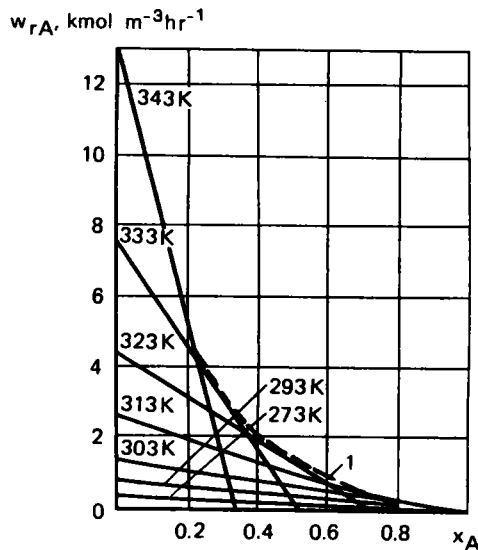


Fig. 10.20 To Example 10.2

Table 10.3 Data for Computation of $\bar{\tau}_{opt}$

Nos.	x_A	$w_{rA,opt}$	$1/w_{rA,opt}$	Nos.	x_A	$w_{rA,opt}$	$1/w_{rA,opt}$
1	0.00	12.8	0.078	12	0.44	1.6	0.625
2	0.04	11.3	0.088	13	0.48	1.3	0.769
3	0.08	9.7	0.103	14	0.52	1.1	0.909
4	0.12	8.2	0.122	15	0.56	0.9	1.111
5	0.16	6.6	0.152	16	0.60	0.75	1.333
6	0.20	5.3	0.189	17	0.64	0.6	1.667
7	0.24	4.2	0.238	18	0.68	0.45	2.222
8	0.28	3.3	0.303	19	0.72	0.35	2.857
9	0.32	2.5	0.357	20	0.76	0.25	4.000
10	0.36	2.3	0.435	21	0.80	0.2	5.000
11	0.40	1.9	0.526				

balance

$$\bar{\tau} = C_{A,0} \int_0^{x_A} dx_A / w_{rA}(x_A)_{opt}$$

will be integrated by numerical methods.

The values of $w_{rA}(x_A)$ spaced $\Delta x_A = 0.04$ apart are given in Table 10.3. The mean residence time $\bar{\tau}$ is given by

$$\bar{\tau} = \Delta x_A \left[\frac{(1/w_{rA})_1 + (1/w_{rA})_{21}}{2} + \sum_{i=2}^{20} (1/w_{rA})_i \right]$$

The optimum mean residence time, $\bar{\tau}_{opt}$, thus found is 0.82 hr. That is, effecting the process along the optimum temperature profile boosts the output by

$$[(1.0 - 0.82)/0.82] \times 100 = \text{approx. } 22\%$$

Maintenance of optimum operating temperatures. How a process can be effected in an industrial-scale reactor at optimum operating temperatures in practice depends on many factors, above all on the enthalpy change on reaction and the reaction kinetics.

Endothermic reactions (both reversible and irreversible) should preferably be effected in reactors with heat input from the outside and with the temperature distributed uniformly enough throughout the reactor volume. The most commonly used type of reactor for endothermic reactions is the tubular reactor not unlike in its structure to the shell-and-tube heat exchanger. In this type of reactor, the reaction vessel proper is a tubular conduit in which the feedstock moves in the plug flow, with the heat-transfer medium (which may be flue gases) moving between the tube

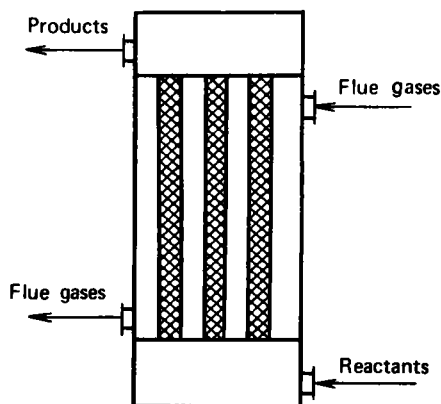


Fig. 10.21 Tubular reactor for endothermic reactions

and the shell. Figure 10.21 shows an example of a tubular reactor intended to effect the steam conversion of natural gas. A similar design is implemented in the retort furnace used to synthesize butadiene from ethyl alcohol — in this reactor the catalyst is loaded into retorts (rather than tubes) which are narrow conduits of rectangular cross-section. In such reactors the conduits for the reaction mixture must be narrow so that the temperature could be uniformly distributed over the cross-section. Under an ideal plug flow, the conditions are the same at any cross-section. In practical reactors, the flow pattern is other than the ideal plug flow, so the temperature at the axis of the conduit differs from what it is at the wall. Figure 10.22 shows approximate temperature profiles over the cross-section in the reactor effecting an endothermic reaction and shown in Fig. 10.21, for two values of conduit diameter. It is seen that in a large-diameter tube the temperature at its axis is markedly lower than it is at the wall. In consequence, the reaction rate in the feedstock moving closer to the tube's axis is lower than the mean reaction rate in the reaction vessel. With catalytic processes, the catalyst may only be applied to the inside surface of the conduits — this will assure a nearly equal temperature throughout the reaction volume.

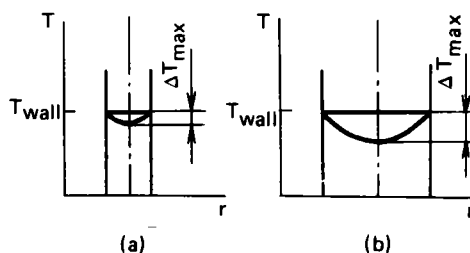


Fig. 10.22 Temperature profiles in (a) small-diameter and (b) large-diameter conduits when effecting an endothermic reaction

Homogeneous endothermic reactions may also be effected in well-stirred reactors with a heat-transfer surface — in this case, too, the temperature will be uniformly distributed throughout the reactor.

Exothermic reactions are as a rule effected in either adiabatic reaction vessels or in vessels with heat abstraction.

In the case of irreversible exothermic reactions, the rise in temperature leads solely to a rise in the process rate. To minimize energy input, such reactions should preferably be effected under conditions when the desired temperature is maintained solely at the expense of the heat released by the chemical reaction and with no heat supplied from the outside. There are two temperature limits — upper and lower — for such a process. The lower limit is the temperature at which the rate of an exothermic reaction (and, in consequence, the rate of heat release) is sufficient for the process to maintain its temperature on its own. Below that temperature, the rate of heat release is lower than the rate of heat removal with the exit stream, and the temperature in an adiabatic continuous reactor will fall.

The upper limit may, among other things, be set by some side effects (which may be side chemical reactions or side physical events). With heterogeneous processes such as the roasting of a particulate solid material, the rise in temperature above a certain limit will cause the particles to fuse together; subsequently this will cause an increase in their time to complete conversion (see Chap. 4) and a fall in reactor throughput. As often, the upper limit is set by the strength of the structural materials used. Of course, stronger materials could be used, but this would involve higher construction costs, which is unattractive economically.

With the exothermic processes involved in microbiological syntheses, the upper limit of temperature is set by the viability of the microorganisms. Therefore, processes in this category should be effected in reactors with heat abstraction. To avoid local heat build-ups, preference should be given to reactors in which the flow pattern is close to perfect mixing. Vigorous agitation in such processes not only assures a uniform distribution of temperature but also speeds up the transport of oxygen from the gas to the liquid phase.

Reversible exothermic reactions should preferably be effected along the optimum temperature profile, that is, with the temperature in the reaction vessel brought progressively down with increasing reactant conversion. This can be done in neither adiabatic nor isothermal reactors. In the former case (under adiabatic conditions) the increase in conversion is accompanied by a release of heat and heat build-up rather than by the cooling of the reaction mixture. In the latter case the temperature remains constant rather than changes with increasing conversion.

It is a formidable task to maintain a process precisely along the optimum temperature profile. This could be done in a plug flow reactor with

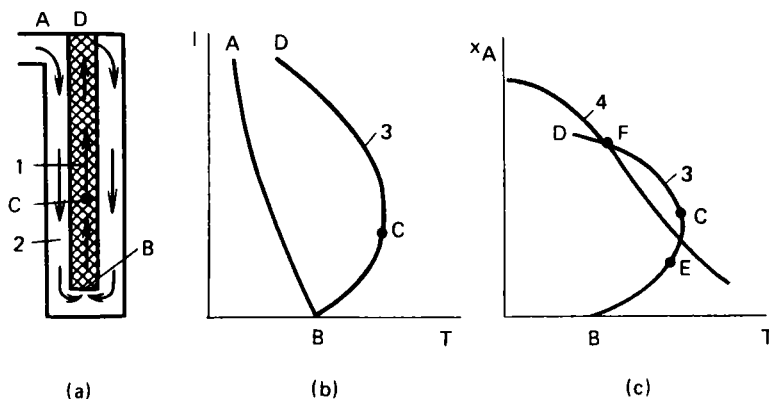


Fig. 10.23 (a) Reactor with a heat-exchange tube; (b) temperature vs reactor length profile; (c) variations in conversion with temperature:
 1, reactor; 2, heat-exchange tube; 3, operating line (variations in temperature over reactor length); 4, line of optimum operating temperatures

a heat-exchange surface on the condition that the quantity of heat withdrawn through the reactor wall is different from one area of the vessel to another. Prior to the reaction, the feedstock should preferably be raised to an elevated temperature and cooled again right upon its entry into the reaction vessel. If we mentally divide such a reactor into segments along its length, then for the process to follow the line of optimum temperatures, the quantity of heat removed within each segment should be somewhat greater than the heat released by the reaction. It should also be recalled that as the fractional conversion increases, the rate of reaction and, in consequence, the rate of heat release fall off. Therefore, within the reactor's segments where the reaction reaches completion less heat should be removed than within the segments at the head of the reactor.

An approximation to the line of optimum temperatures is achieved when a process is effected in a plug flow reactor enclosed in a tubular heat exchanger using a coolant. This type of reactor is shown in Fig. 10.23a. This design, for example, is embodied in the Field tubes employed in ammonia synthesis reactors (ammonia converters). Figure 10.23b shows how the temperature varies along the length of the reactor, and Fig. 10.23c illustrates the manner in which the temperature varies with changes in the fractional conversion of the reactants.

The operating line which shows how the temperature varies with increasing conversion (curve 3) within the portion *ECFD* runs very closely to the optimum temperature profile (curve 4). However, this type of reactor falls short of meeting the requirements with regard to heat transfer. To demonstrate, the rate of heat release within region *BC* is at a maximum,

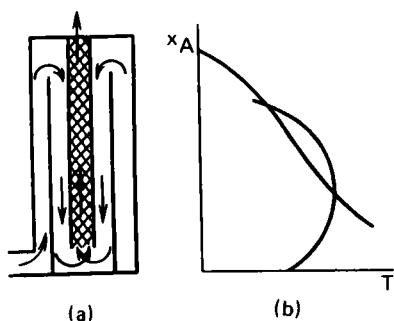


Fig. 10.24 (a) Reactor with double heat-exchange tubes and (b) temperature profile in it

and a good deal of heat has to be removed. However, the rate of heat removal within this region is small because the driving force of heat transfer, ΔT , is likewise small. Within the region FD a relatively small quantity of heat is released, but the outer tube passes a cold gas, so the driving force ΔT is high, and the rate of heat removal is greater than needed. This drawback may to some extent be remedied in a similar reactor using double heat-exchange tubes (Fig. 10.24).

Generally, the approximation to the optimum temperature profile is considered in practice to be satisfactory if the reactor meets the following condition:

$$w_r \geq 0.8w_{r,opt} \quad (10.63)$$

The plot of $x_A(T)$ shows two lines answering the equality

$$w_{rA} = 0.8w_{rA,opt}$$

one running above and the other below the optimum temperature profile. The two lines thus bound an *optimum temperature region* (see, for example, Fig. 10.18), which satisfies the condition defined in (10.63). When plotting the optimum temperature region it is important to remember that the upper boundary lies below the equilibrium curve, $x_{A,e}(T)$. When choosing a reactor and its operating conditions, it is important to assure that the greater portion of the operating line lies within the optimum temperature region. This condition is satisfied, for example, by the operating lines shown in Figs. 10.23c and 10.24b.

A relatively simple way of coming very nearly to optimum temperature conditions is to effect the process involved in a multistage plug flow reactor in which each stage operates adiabatically, and some heat is removed between the stages (Fig. 10.25a). Figure 10.25b shows the operating line of such a reactor. In the first stage the process is effected adiabatically, and the changes in temperature and conversion are related by Eq. (10.49).

The volume of each stage should be such that the fractional conversion at its exit, $x_{A,1}$, corresponds to the intersection of the adiabatic path with the upper boundary of the optimum temperature region. The required

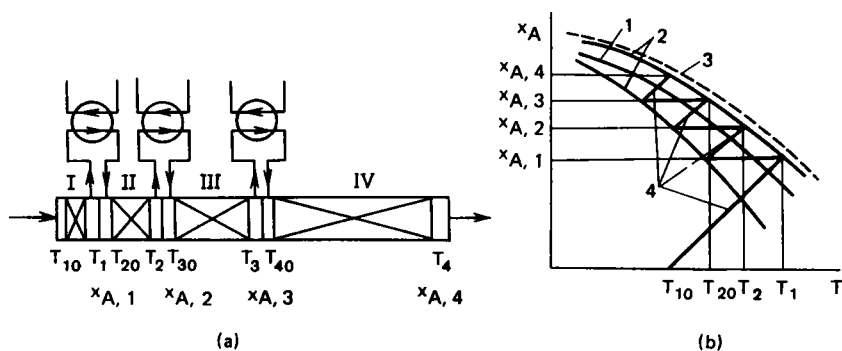


Fig. 10.25 Multistage plug flow reactor: (a) inter-stage heat removal and (b) the course of the process:

1, line of optimum operating temperatures, $w_{rA} = w_{rA,opt}$; 2, $w_{rA} = 0.8 w_{rA,opt}$; 3, equilibrium; 4, operating line

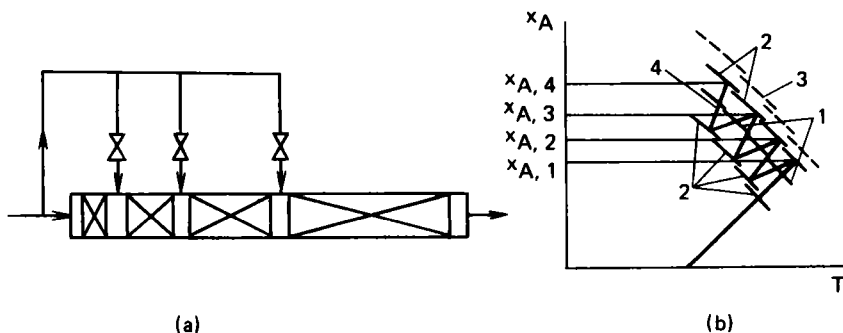


Fig. 10.26 Multistage plug flow reactor with bypass lines to admit cold gas between stages: (Notation is the same as in Fig. 10.25)

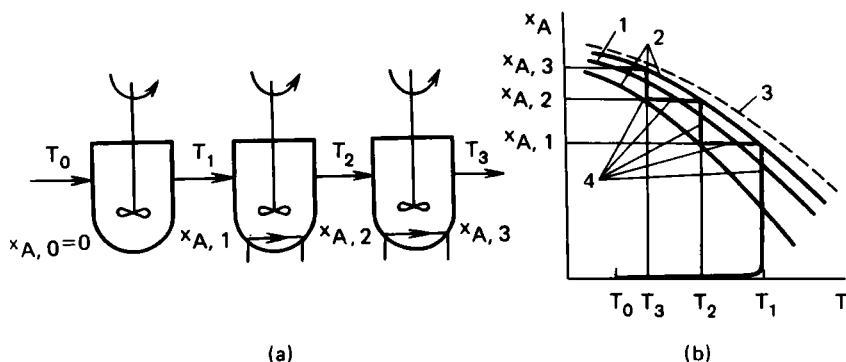


Fig. 10.27 A cascade of perfectly mixed tank reactors: (a) heat removal from stages and (b) the course of the process. (Notation is the same as in Fig. 10.25)

volume (or mean residence time) can be found by solving the set of material and heat balances of the reactor.

The reaction mixture leaving stage *I* is cooled from temperature T_1 to temperature T_{20} corresponding to the lower boundary of the optimum temperature region at $x_A = x_{A,1}$. Then the feedstock passes through adiabatic stage *II*, a second heat exchanger, stage *III*, and so on. Since the rate of reaction decreases with increasing fractional conversion, every next stage should have a progressively larger volume.

Between the stages of an adiabatic reactor the reactants can be cooled not only by indirect heat transfer, but by injecting an amount of fresh cool feedstock. This approach is illustrated in Fig. 10.26*a*. In the general case, the addition of fresh feed to the partly reacted mixture changes the reactant concentration and may cause a shift in the position of equilibrium. Since the position of the optimum temperature profile also depends on the position of equilibrium, it follows that a change in the equilibrium composition will somewhat shift the position of the optimum temperature profile as well. This situation is shown in Fig. 10.26*b*.

An alternative way of approximating optimum operating temperatures is to effect the process in a cascade of stirred-tank reactors, where a temperature of its own is maintained in each tank through provision of heat-exchange surfaces. This type of reactor system is illustrated in Fig. 10.27*a*. Having chosen temperature T_1 and, in consequence, the fractional conversion in the first unit, $x_{A,1}$, so that they correspond to the upper boundary of the optimum temperature region, we can compute the required volume for the 1st tank, treating it as a constant-temperature reactor. The 2nd and 3rd tanks can be assessed in a similar way. Proceeding from the heat balances over such reactors, we can find the heat-exchange surface area and the flow rate of coolant required to maintain each tank at the temperature determined by the operating line shown in Fig. 10.27*b*.

In each case examined above, the process may be further optimized in terms of unit volume, initial temperature, volumetric throughput (flow rate) in the bypass lines, etc. The objective of this optimization is to obtain the most attractive economic performance of the process. In more detail, problems of optimization are examined in the literature on the subject.*

Unsteady-state catalytic reactions at optimum operating temperatures. Recently, there has been a growing interest in unsteady-state catalytic processes among those concerned with catalysis. At least two motives behind

* See, for example A.I. Boyarinov & V.V. Kafarov, *Optimization Methods in Chemical Engineering*; G.V. Reclaitis, A. Ravindran & K.M. Ragsdell, *Engineering Optimization. Methods & Applications*. John Wiley & Sons, Inc. New York—Chichester—Brisbane—Toronto—Singapore, 1983.

this interest may be noted. Firstly, many catalytic processes are of an unsteady-state nature — the catalytic activity changes with time due to the effects of the reaction medium. Secondly, it has been found that a deliberately induced unsteady state may enable in some cases optimal process conditions to be achieved in reactors or systems of a simpler design.

As will be recalled, in a steady state the process variables remain time-invariant, notably the composition and temperature of the gas phase in the reactor and the concentrations of all the intermediates at the surface. In this case, the rate of a catalytic process will likewise be in a steady state — it will solely be decided by the composition of the reaction mixture in the gas phase and the temperature of the catalyst:

$$w_{rA} = w_{rA}(C_A, C_B, C_R, C_S, \dots, T)$$

In unsteady-state processes the composition of the gas phase and the temperature of the catalyst vary with time. The material and heat balances over a catalyst grain or the catalyst bed as a whole include time derivatives of composition and/or temperature (accumulation of mass or heat). In the circumstances, the observed rate of chemical transformation, W , found by solving a system of differential equations and from initial conditions, is not equal to $w_{rA}[C_i(\tau), \dots, T(\tau)]$. The faster the change in the composition of the gas phase and catalyst, the greater the difference between w_{rA} and W .

Four basic causes of an unsteady state may be named for heterogeneous catalytic processes, namely:

- (1) Forced external actions.
- (2) An unstable steady state or self-maintained oscillations.
- (3) Random interference and disturbances.
- (4) Changes in catalyst activity and specificity with time.

It is far more difficult to build models for unsteady-state processes and, especially, to do computations on the basis of such models by numerical methods, and to set up automatic process control systems than for steady-state processes. What follows is only a brief outline of the qualitative effects of some forms of an unsteady state in catalytic processes.

Operation in the presence of forced external actions has as one of its results that, given the same mean values of input variables, but different time dependences, there is a much wider choice of concentration, temperature and composition fields forming at the catalyst surface. That is why operation under unsteady-state conditions may favour the process better than operation under steady-state conditions. For example, the throughput and selectivity of the process under unsteady-state conditions may turn out to be far more higher than they are under steady-state conditions. This difference, arising above all from the nonlinear relationship between the reaction rate and the composition of the reaction mixture, depends to a great

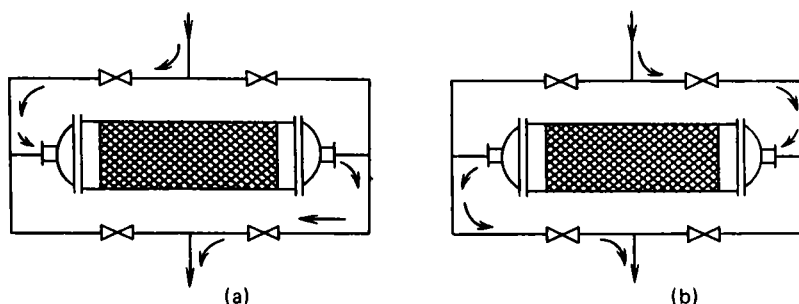


Fig. 10.28 Adiabatic catalytic reactor with a periodic feed flow reversal

extent on the dynamic properties of the catalyst surface. The efficiency of an unsteady-state process depends on the manner in which the input variables (reaction mixture composition, initial temperature, and duty) change.

As an example, we will dwell on a reversible exothermic reaction effected in an adiabatic reactor with a deliberately induced unsteady state. This is brought about by a periodic reversal of the feed flow through the catalyst bed (Fig. 10.28).

The rationale of the method is that, in addition to its principal role of speeding up the reaction, the catalyst bed acts as a heat regenerator.

At start-up, the fixed catalyst bed is raised to a temperature at which the exothermic reaction in question can proceed at a high rate so that the rate of heat release is likewise high. Following that, a substantially cooler stock is fed to the reactor (Fig. 10.28a). Since the catalyst has already been heated, the reaction proceeds at a sufficiently high rate, and a well-defined temperature profile moving with time is established along the catalyst bed. Gradually the temperature within the inlet portion of the catalyst bed falls off and that within the outlet portion remains unchanged at a rather high level or rises still higher. At some instant, the flow of fresh feed is reversed (Fig. 10.28b), and the thermal front begins to move in the opposite direction.

Although the temperature at the inlet to the catalyst bed is low, the unsteady-state reaction is kept going because the high-temperature portion of the bed continuously receives a stream of reaction mixture containing an unreacted reactant which undergoes a chemical transformation and releases heat in that region. Some of the reaction heat is conserved within the reaction volume. The extended surface of the catalyst grains provides for a good heat transfer from the hot catalyst to the cold gas stream so that the temperature of the latter is raised high enough for the reaction to progress.

Figure 10.29 shows the temperature and conversion versus catalyst-bed

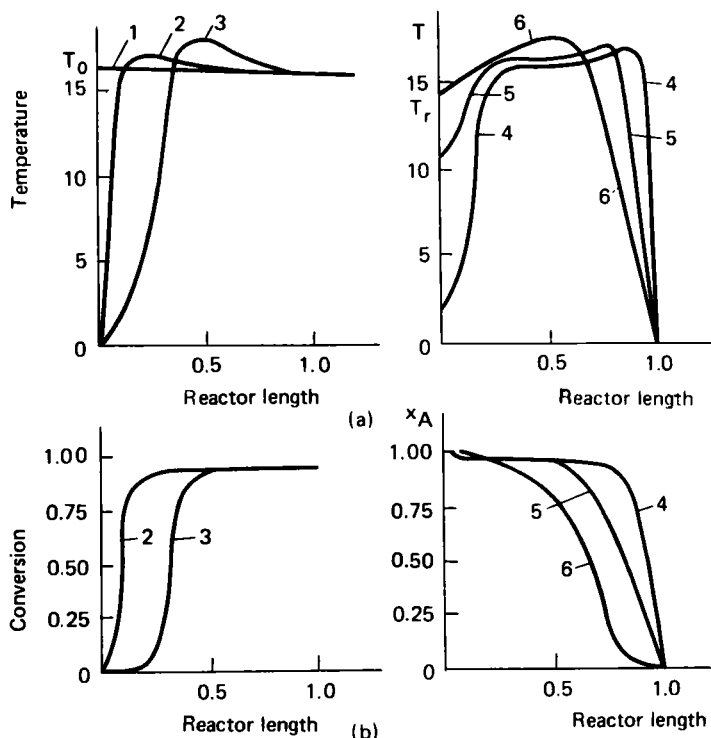


Fig. 10.29 Profiles of (a) temperature and (b) fractional conversion as a function of distance z along a catalyst bed operating under unsteady state conditions at different instants:

1, τ_1 ; 2, τ_2 ; 3, τ_3 ; 4, τ_4 ; 5, τ_5 ; 6, τ_6
 Temperature and reactor length are given on a per-unit basis

length profiles deduced for the above unsteady-state reactor effecting a 1st-order reversible exothermic reaction, $A \rightleftharpoons R$.

Let, prior to start-up, the temperature of the catalyst bed be the same over the entire length and equal to T_0 (curve 1). At time $\tau_1 = 0$, a reaction mixture is admitted to the catalyst bed at temperature T_{in} . Curves 2 and 3 are the temperature and conversion profiles at the subsequent instants τ_2 and τ_3 . The left-hand portion of the bed gradually cools off. At time τ_3 the flow of reaction mixture is reversed. From this instant on, the right-hand portion of the bed, now at the inlet end of the reactor, begins to cool off, and the high-temperature region is shifted to the left (curves 4 and 5). The temperature at the outlet from the catalyst bed rises, but does so slowly owing to the thermal capacitance of the catalyst. The flow of reaction mixture is again reversed at time τ_6 when the temperature at the exit from the catalyst bed has risen to T_r (the reversal temperature). The thermal front

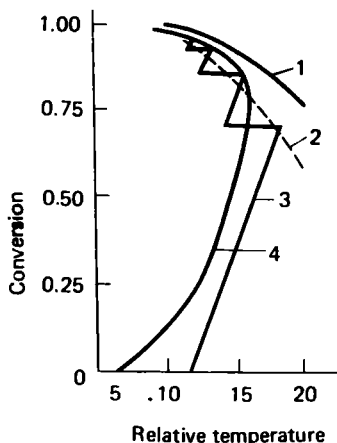


Fig. 10.30 The x_A -vs- T diagram for the reversible exothermic reaction $A \rightleftharpoons R$:

1, equilibrium curve; 2, line of optimum operating temperatures; 3, operating line of the process effected in a reactor with consecutively arranged catalyst beds and intermediate heat removal; 4, operating line of the process effected in a reactor with a single catalyst bed under unsteady-state conditions

again begins to move from left to right. When the temperature at the outlet from the catalyst bed reaches T_r , the flow of reaction mixture is reversed again. The subsequent temperature and conversion profiles are similar to curves 4, 5 and 6, that is, alternatively go from left to right or from right to left. A periodically recurring autothermal condition is established in the catalyst bed: the quantity of heat brought along with the reaction mixture over a cycle plus the heat released over the same cycle is equal to the quantity of heat removed from the catalyst bed by the exit stream.

As is seen from Fig. 10.29, the exit temperature profiles (curves 4, 5, and 6) run progressively lower as the fractional conversion is increased. This implies that the process is effected at optimum temperatures. Through a proper choice of reversal temperature, linear velocity, catalyst grain size and inlet temperature, it is possible to come very closely to the line of optimum temperatures and, as a consequence, to obtain a high degree of conversion and a high throughput from a single catalyst bed.

Figure 10.30 shows an optimum temperature profile (curve 2) which provides for a maximum attainable rate in an exothermic reversible reaction, $A \rightleftharpoons R$. Line 3 applies to a process effected traditionally in a steady-state reactor which uses several consecutively arranged catalyst beds and intermediate heat removal (compare Fig. 10.25). The theoretically optimum performance calls for a reduction in temperature with increasing conversion, but the situation is just the opposite in an adiabatic catalyst bed operating under steady-state conditions. Curve 4 depicts the situation existing in a single adiabatic catalyst bed which operates under unsteady-state conditions and assures an overall degree of conversion comparable with that obtained in a steady-state reactor operating as depicted by line 3.

Part Three

GENERAL PRINCIPLES OF CHEMICAL PROCESS DESIGN

Chapter Eleven

RAW MATERIALS AND ENERGY SUPPLY FOR THE CHEMICAL PROCESS INDUSTRIES

The chemical process industries treat huge quantities of raw materials and consume large quantities of water, fuel, and energy. In many industrial chemical processes, it takes 3 or 4 tonnes of raw materials to turn out one tonne of product; in some cases this figure may be as high as 5 or 6 tonnes. If we recall that the needs of any nation in chemical products increase with every year, it becomes apparent how important it is to search for ever new sources of raw materials, fuel, and energy and how essential it is to expand the range of chemical products made from ever cheaper and better starting materials.

The effective utilization of raw materials and energy in chemical processing is one of the pivotal tasks facing the chemical process industries.

11.1 Raw Materials for the Chemical Process Industries

From the view-point of raw materials, the chemical process industries stand out in more than one respect. For one thing, the same process may draw upon several different supplies of raw materials which may include naturally occurring minerals and substances, agricultural products, air, and water. For another, the same raw material may be used to turn out a range of products. Finally, more than one chemical treatment may be used to derive a wide gamut of products from the same starting material. For example, benzene is the starting material for man-made rubber, polystyrene, caprolactam, pesticides, and many other products. On the other hand, the many manufacturing or processing methods available allow one and the same product to be obtained from different raw materials. For example, acetylene can be produced from natural gas, petroleum refinery off-gases, casing-head gases, and calcium carbide.

Most chemicals can be produced in more than one way. Sulphuric acid, for example, can be manufactured by the contact process and the Glover tower process; ethyl alcohol can be produced by the vapour-phase process and sulphuric-acid hydration, etc.

Starting materials for the chemical process industries may come from mining, the petroleum and gas industries, the pulp and paper industry, fer-

rous and non-ferrous metallurgy. Among those coming from ferrous metallurgy are aromatic hydrocarbons, naphthalene, anthracene, phenols, cresols, sodium rodanide, and sulphur dioxide, the latter being a very valuable raw material for the manufacture of sulphuric acid. Especially large quantities of sulphur dioxide are recovered from the waste (or flue) gases formed when roasting copper, zinc, lead ores and concentrates. The recovery of waste gases is very beneficial from an economic point of view — with no added cost of roasting a sulphur-bearing material it permits the production of over 10 tonnes of sulphuric acid per tonne of copper smelted.

Agricultural raw materials also play a role in the chemical process industries but their share is steadily decreasing. Taking the USSR as an example, more than 4.5 million tonnes of food-grade products is saved every year now that alcohols, synthetic acids, glycerine and detergents formerly manufactured from food-grade materials are being produced from other sources.

The overall trend in the chemical process industries is towards a fuller, preferably comprehensive utilization of materials, including those low in the valuable component(s), recovery of wastes within the chemical and other industries, and a better processing of ever larger amounts of natural substances, such as petroleum, gases, coal, shales, wood, and the resources of the oceans and seas. Thus, the change-over from natural hydrocarbons to coal will eventually expand the supply of raw materials and energy more than ten-fold.

In the nearest future a large group of products will be mainly synthesized from carbon monoxide and methanol. Already now methanol is widely being used for the industrial manufacture of acetic and formic acids, formaldehyde and formaldehyde-based thermosetting plastics, ethers, esters, chloromethanes and methyl amines. It is also gaining ground in the manufacture of traditional petrochemicals.

With a multiple choice of resources, there is a broader and more reliable basis for the expansion of the chemical process industries, as it can be planned according to the availability of mineral deposits, as well as the economic and technical aspects of their development and exploitation.

Basic concepts and classification. Chemical processing involves starting (raw or source) materials, semifinished or intermediate products (or simply intermediates), and end products (or simply products).

Intermediates result from the chemical processing of raw or source materials and serve, in turn, as starting materials for the manufacture of other products. In practice, however, any intermediate is in fact the end product for a given plant and a source or starting material for another plant acting as its consumer. For example, the sulphuric acid manufactured

at non-ferrous integrated works is an end product for the latter but a starting or source material for the manufacture of fertilizers, notably phosphate fertilizers.

Of all the elements in the Periodic Table, only 60 are of practical interest to the chemical process industries at present, with their share to the overall activity ranging from a few kilograms to tens of millions of tonnes. In fact, tonnage chemical processes base themselves on a very limited number of raw materials, but use them in large quantities (sulphur and its compounds, apatite and phosphate rock, natural gas, petroleum, coal, limestone, common salt, water, air, and a few more).

By processing sulphur, pyrite, limestone, common salt, phosphates, polymineral ores, natural gas, casing-head gas, coke-oven gas, and atmospheric nitrogen, the chemical process industries turn out sulphuric, nitric, phosphoric acids and synthesized ammonia for the manufacture of nitrogen, phosphorus, potash, and complex (or complete) fertilizers, caustic and calcined soda, and mineral salts. Natural gas is used as the source material for heavy organic syntheses, the manufacture of fertilizers, plastics, synthetic rubber, chemical fibre, pharmaceuticals, etc.

Petroleum is a most valuable raw material for the production of fuels, lubricants, synthetic fibre, synthetic rubber, plastics, detergents, and a multitude of other products.

Raw materials for the chemical process industries may be classed in more than one way as follows:

- according to origin, into mineral, vegetable, and animal;
- according to reserves, into nonrenewable (ores, minerals, and fossil fuels) and renewable (water, air, vegetable and animal materials);
- according to chemical composition, into inorganic (ores and minerals) and organic (oil, coal, natural gas);
- according to state of matter, into solid (ores, minerals, coal, shales, and peat), liquid (water, brines, oil) and gaseous (air, natural gas).

Furthermore, raw materials may be classed into primary (minerals, those of vegetable and mineral origin, fossil fuels, water, and air) and secondary (industrial and consumer wastes); into natural and man-made (coke, chemical fibre, synthetic rubber, synthetic dyestuffs, synthetic resins, etc.).

Mineral raw materials include ores (or metallic raw materials), non-ore materials, and combustible (or organic) materials. Ore raw materials are iron, copper, chromium, titanium and other ores bearing mainly oxides and sulphides of metals. Ores containing compounds of several metals are called polymetallic. Non-ore raw materials are common salt, phosphate rock, apatite, gypsum, limestone, sand, clay, asbestos, mica, sulphur, etc. Combustible materials, or fossil fuels, are peat, brown, bituminous and anthracite coal, shales, and natural gas. They consist of organic com-

pounds and may be used as source materials for the manufacture of other materials or products and for power generation.

Vegetable raw materials (sunflower seeds, potatoes, sugar beet, wood, cotton, flax, hemp, rubber-yielding plants, corn cobs, husks of sunflower seeds, rice, and cotton, etc.) and animal raw materials (wool, natural silk, pelts, hides, oils and fats, milk, etc.) are processed into foodstuffs (food-grade raw materials) or into household or industrial products. Thus, vegetable fats and oils are used in the manufacture of soap, paints and varnishes, finishing agents for leather and fabrics, and starches in the textile industry. Corn cobs and husks of sunflower, rice and cotton seeds are widely employed in the microbiological industry as raw materials for the production of feed-grade proteins, furfural and xylite.

The raw materials used in the chemical process industries are to meet several requirements which may be summed up as follows.

(1) They should call for a minimum number of processing steps in order to be converted to an end product.

(2) They should be in a state of matter which requires the least possible expenditure of energy in order to bring them to a condition essential for the chemical reaction to take place.

(3) They should possess a maximum of energy, which means that they should dissipate as small a fraction of the original energy as practicable.

(4) They should be amenable to a high degree of processing and involve the least possible losses of energy with side streams and by-products.

(5) They should need the lowest possible level of temperature, pressure and energy input for phase changes so that the utility requirements of a given process can be held to a minimum.

(6) The concentration of the end product in the reaction mixture should be a maximum.

Secondary material resources. These are an important source of raw materials for the chemical process industries. They include production wastes, consumption wastes, and by-products.

Production (or industrial) wastes. This refers to what is left over from the raw (or source) materials used after they have been processed into products. They will usually have lost a major part or all of their qualities and no longer measure up to applicable standards or specifications. Yet, given some form of re-processing (or even without it), they may be reclaimed for use in some other field of manufacture or consumption.

Consumption wastes. This refers to a range of products and materials that have worn out from use to a point where it is not economical to reclaim them. Examples are machines removed from service, broken or damaged glassware, rubber and plastic products, spent reagents and catalysts (they may collectively be referred to as industrial consumption

wastes), and also worn or broken household goods and personal items (they may be classed as household consumption wastes).

By-products. These are substances or products obtained during the processing or manufacture of some other substances classed as the desired products, but are not the goal of a given manufacture. As a rule, however, they may be used as end products in their own right. In most cases, they are a marketable merchandise. In fact, they are expected to meet certain specifications, they have a market price, and their output is usually planned. The mining and/or beneficiation of raw materials leaves what may be called associated products or co-products (an example is associated petroleum gas). By-products and co-products from one process are as a rule end products for some other manufacture.

Secondary material resources may replace primary materials in part or even fully in the manufacture of marketable goods. In this case, the chemical process industries act not only as a consumer of natural resources, but also as their saver.

In the petrochemical industry, secondary resources are various hydrocarbon components, spent catalysts, and spent reactants. In Soviet practice, their recovery saves at least 20-25% of the raw and source materials used up.

Examples of tonnage production and consumption wastes are phosphogypsum, pyrite cinder, ferrous slag, ash from thermal power stations, lignin, waste paper, glass scrap, apple squash, etc.

11.2 Rational and All-Round Utilization of Material Resources

It is economically important to utilize material resources in a rational and all-round way, for industry today uses huge and ever increasing quantities of natural materials.

In the past 80 years, the quantity of fossil materials mined from the Earth's crust has increased many times over what had been produced during all of the history of our civilization. The 20th century claims 85% of all copper, 87% of all iron ore, 90% of all coal, and 99.5% of all petroleum ever mined. Of this amount, a predominant part was mined in 1961-1980. The figures for this period are as follows: coal, over 40%; iron ore, nearly 55%; petroleum, over 73%; gas, over 77%; bauxites, 80%. World output has increased 1.4 times for coal, 1.8 times for iron ores, 2.6 times for potash, 3.2 times for phosphorites, 2.9 times for petroleum, and 3.2 times for natural gas.

The total quantity of rock mined and processed runs into many thousand million tonnes. Taking the USSR as an example, it has to handle more than 2 thousand million tonnes of rock every year to make its non-ferrous metals. In 1985, the world's production of the key materials was as follows

(in million tonnes):

Petroleum (including gas condensate)	2 664
Coal	4 273
Natural gas (thousand million m ³)	1 614
Cement	934
Steel	712
Fertilizers (in terms of 100% nutrient)	142
Synthetic resins and plastics	72
Chemical fibre	16

At this writing, a mere 10% of the original resources is utilized in the end products, and the remaining 90% is irrecoverably lost.

With industrial production expanding at an ever increasing rate, the unrenewable natural sources of raw materials are exhausted to an ever greater extent so that miners have to work deposits of a progressively lower value or occurring at a progressively greater depth, lying in uninhabited and remote areas. As more effort has to be put into prospecting, exploration and development of mines or fields, more money has to be spent to turn out one money unit's worth of marketable products.

An instructive example is offered by phosphate rock used in the manufacture of phosphorus fertilizers. In 1970 one had to process 26.7 tonnes of rock to make 1 tonne of P₂O₅. In 1975 the figure rose to 30.5 tonnes, in 1980 to 34.9 tonnes, and in 1985 to 41.6 tonnes.*

This is also true of other products of mining. Notably, petroleum and natural gas, both of which are at present the principal sources of power and raw materials for the manufacture of nitrogen fertilizers and practically all organic compounds, have to be largely produced in remote areas, from large depths, and even offshore. In recent years, the cost of petroleum production in the Soviet Union has doubled, that of gas has increased by a factor of 2.5, and that of coal has risen 1.5 times.

What is meant by the rational utilization of mined raw materials is the recovery of all their values and the utilization of wastes. When this goal is achieved, the return on investment is high and environmental pollution is held to a minimum.

The all-round utilization of raw materials implies the recovery of all by-products and wastes and their conversion into marketable merchandise as well as the integration of several processes within a single industrial entity. For example, in addition to hydrogen (for ammonia synthesis), the reforming of natural gas yields also carbon dioxide which is not utilized in ammonia synthesis. Therefore, it is customary to integrate ammonia synthesis

* Where not otherwise stated, the figures quoted in the text apply to the situation in the USSR. — *Translator's note.*

with urea manufacture which is the user of carbon dioxide:



The all-round utilization of raw materials is widely practised in the processing of solid fuels (coal and shales), petroleum, non-ferrous ores, mined chemicals, and vegetable materials. For example, in the by-product coke industry the comprehensive utilization of coal produces coke as the main end product and also coke-oven gas and tar; when suitably processed, the coke-oven gas and tar can be converted to many organic compounds or directly used as source materials by the nitrogen industry. The processing of petroleum, natural gas, and associated petroleum gas may yield, for example, high-quality sulphur (99.00% S) and a range of other products. The Soviet Union has plants that derive helium of 99.985-99.995% purity from natural gas.

As applied to non-ferrous concentrates, comprehensive utilization yields large quantities of the metals cadmium, indium, bismuth, rhenium, selenium, tellurium and other scattered elements. The waste gases of non-ferrous metallurgy serve as source materials for sulphuric acid (the acid thus produced accounts for more than one-quarter of the total output in the USSR).

As has been noted, the use of secondary material resources saves the traditional materials and serves to minimize environmental pollution. For example, phosphogypsum may advantageously be used to improve black alkali soils, as an additive to cement, and in the manufacture of gypsum binders, sulphuric acid and cement. Halite wastes are promising and economically attractive to use in the preparation of common salt, both food- and technical-grade. Pyrite cinder could fully be utilized in the preparation of iron-ore pellets for ferrous metallurgy and in the smelting of non-ferrous, rare and noble metals. Ash, cinder and slag may be used to make cement, brick, concrete additives, and other building materials. Slags from iron and steel manufacture are good source materials for cement, mineral wool, slag pumice, and other materials.

As applied to apatite-nepheline rock, comprehensive processing can yield alumina, soda products, fluorides, Portland cement, titania, and rare-earth compounds.

In recent years, advances in science and technology have added many more wastes to those recovered, reclaimed or otherwise re-processed commercially.

Again taking the USSR as an example, the list of fully or partly re-processed wastes contains over 250 names, including tonnage ones such as molten slag from the phosphorus industry, used to make granulated slag, slag wool, pumice, glass ceramics, crushed slag, etc.; fluorine-bearing liquors from the manufacture of single and triple superphosphate and wet-

process phosphoric acid. These liquors are treated to recover silicon fluorides, aluminium fluoride, and sodium fluoride, instead of using the naturally occurring fluorspar. Some wastes, such as off-gas hydrochloric acid, hydrogen chloride, bisulphite liquor, phosphate rock screenings, and wastes from the manufacture of polyamide, polyester and polyacrylonitrile fibres are re-processed and reclaimed completely.

To sum up, the rational and all-round utilization of raw materials, including secondary material resources, goes a long way towards meeting a country's economic needs for staple and associated industrial products and offers a sizeable economic benefit in terms of reduced losses, a better supply of raw materials, better economic and technical performance, reduced environmental pollution, better use of the Earth's resources, and the conservation of deposits and water resources.

11.3 Beneficiation of Raw Materials

The beneficiation of raw materials is an arrangement of physical and physico-chemical methods for the treatment of ores, coal, and other fossil minerals in order to remove the worthless material (called the gangue) and to collect their valuable constituents (minerals) into products (concentrates).

When a raw material contains several valuable constituents, it is separated into fractions, each high in a particular component which is then utilized as the source material for some manufacture.

Raw materials can be beneficiated in more than one way. With solids, the following methods are used.

Gravity methods. For their effect, these forms of separation depend on the difference in settling velocity between the particulate constituents varying in density (specific gravity) and size present in a stream of liquid or gas, or on centrifugal force. These methods are widely used to dress raw materials in the manufacture of silicates, mineral salts, and metallurgy.

Electromagnetic separation. Here the separation is based on the difference in permeability. It can be used to separate magnetite, chrome iron ore, rutile and other magnetically susceptible materials from the gangue.

Electrostatic separation. This method utilizes the difference in electric conductivity for the separation of current-conducting constituents from dielectrics, such as gypsum, limestone, etc.

Flotation. In this form of separation, the feed is a suspension of relatively fine particles in a liquid (technically known as the pulp). The constituents are separated from one another or some solid particles are extracted from the pulp stream owing to their ability to attach themselves to air bubbles that are forced into the feed. The bubble-particle aggregates are carried (or float) to the surface where a froth rich in the desired mineral is formed.

Flotation uses various flotation agents added to the pulp in small amounts. Some serve to build up a finely dispersed and stable froth and are called *frothers*. Others promote the attachment of particles to air bubbles and are referred to as *collectors*.

Practically all minerals can be separated from the gangue by flotation. In fact, flotation today is one of the most commonly used, versatile and perfect methods of beneficiation used on a commercial scale.

Liquid solutions are concentrated by evaporating the solvent, freezing out the desired constituent, or by causing the impurities to precipitate or to pass into the gas phase.

Gas mixtures are separated by means of the consecutive condensation of the gas components as they are compressed and the temperature of the mixture is brought down.

The beneficiation of raw materials is a vital element in energy-saving technology.

11.4 Water and Air in the Chemical Process Industries

The chemical process industries are among the leading consumers of water and air. These two materials are used in nearly all chemical processing for a large variety of purposes. Chemical factories today use up between them as much as 1 million cubic metres of water per day. Water is used to produce hydrogen and oxygen, to dissolve solids, liquids and gases, as a reaction medium, an extractive agent, an absorbent or a carrier, to heat and cool materials and pieces of equipment, to form pulps and slurries, to wash products and plant items, etc. Also, it is widely used as the working fluid in hydraulic, thermal and nuclear power stations.

All water present on the Earth totals about 1500 million km³. Our planet's hydrosphere accounts for 70.8% of the Earth's total surface area, or 361 million km². This is 1370 million km³ in volume. The greater proportion of this water is in a continuous movement through the hydrologic cycle under the action of the heat coming from the Sun and from the planet's insides.

Usable fresh water from water bodies accounts for a mere 0.3% of the hydrosphere by volume. More important economically is river water. This is because, above all, the rivers carry fresh water and span huge distances. Historically it has so happened that most cities, towns and other communities are situated at the river banks. The instantaneous reserves of water in all of the globe's rivers is about 1200 km³, and this volume is renewed every 12 days on the average.

At this writing, a total of up to 170 km³ of water per year is used up in the world for the various needs (irrecoverable losses).

11.4.1 Classification of Natural Water and Characteristics of Its Impurities

Natural water is usually classed into atmospheric, surface, and ground (subsurface or subterranean).

Atmospheric water falls out as rains or snow and carries negligible amounts of impurities. These impurities mainly are dissolved gases (O_2 , CO_2 , N_2 , etc.), salts, bacteria, etc. Atmospheric water is the source of water supply in arid regions.

Surface water refers to the water flowing in rivers and canals and held in oceans, seas, lakes, and water reservoirs. It contains a wide range of inorganic and organic substances, depending on the climatic, geomorphological, soil, and geological conditions, man's agricultural and hydraulic-engineering activities, the impact of industry, and some other factors.

Special mention should be made of *seawater*. It is a multicomponent solution of electrolytes and contains all the elements present in the Earth's crust. The solutes present in seawater are many salts (up to 2.6% by mass sodium chloride, magnesium chloride and sulphate, etc.) and also atmospheric gases (nitrogen, oxygen, and carbon dioxide). Water from one sea or ocean differs from that from any other in both the overall concentration and make-up of salts.

Groundwater is that which comes from artesian wells, water-table wells, springs, and geysers. It carries appreciable amounts of mineral salts leached out of soil and sedimentary rock, and small amounts of organic substances.

Another way to class water is according to its salt content. Thus we have fresh water which carries up to 1 g of salts per kilogram of water; brackish water with 1 to 10 grams of salts per kilogram, and saline water with over 10 g of salts per kilogram.

Still another way to differentiate between various kinds of water is according to the anion it contains. Thus, there is hydrocarbonate water in which the prevailing anion is HCO_3^- or the sum of HCO_3^- and CO_3^{2-} anions; sulphate water; chloride water, etc.

Natural water is a complex dynamic system which contains gases, inorganic and organic substances present in true solution form, in colloidal form, or in suspension.

Those present in true solution form are mainly the inorganic salts that enrich water with the Ca^{2+} , Mg^{2+} , Na^+ and K^+ cations and the SO_4^{2-} , CO_3^{2-} , HCO_3^- , and Cl^- anions. These ions find their way into water from soil and rock. Some organic compounds and the dissolved gases (CO_2 , O_2 , H_2S , etc.) may be present as undissociated molecules. The solubility of gases in water depends on temperature, pressure, and the ionic makeup of the other substances dissolved.

Those present in colloidal form are undissociated or slightly dissociated compounds of aluminosilicates, iron silicates, iron hydroxide, silicic acid, and various organic substances. Organic colloids mainly consist of humic acids, fulvic acids, lignin, protein, cellulose, various resins, and other complex compounds. Those present in suspension are particles of clay, sand, limestone and gypsum. Natural water may also carry some living organisms, such as bacteria, fungi, algae, coquins, etc.

Natural water is continuously changing in composition. This is favoured by redox reactions, by mixing of water from different sources, by the fact that the dissolved salts may be precipitated due to changes in temperature and/or pressure, the coarse particles may be allowed to settle or be stirred up again, the soil and water may exchange ions, and the microbiological processes may enrich water with microelements.

There is a further arbitrary subdivision of water into *industrial* and *drinking* or *potable*. The impurity content of each category is subject to applicable regulations.

Water quality is determined by physical, chemical, and bacteriological tests. It is customary to describe water quality in terms of smell, taste, clarity (or turbidity), colour, temperature, suspended solids content, total solids content, total and constituent alkalinity, chemical oxygen demand, and pH value.

The suspended solids test tells us what fraction of the total solids present in a water sample is present as suspensions of clay, sand, and soil. Numerically it is expressed in milligrams per litre on a dry mass basis.

The total solids test quantifies all the solids in a water sample, both inorganic and organic, suspended and dissolved, in true solution and in colloidal form. This parameter is found by evaporating a water sample to dryness and weighing the residue. The total quantity is expressed as milligrams per litre on a dry-mass-of-solids basis.

Once a sample has been dried and measured, the organic content of both total and suspended solids can be determined by firing the residue at a specified temperature and for a specified span of time. The remaining material will represent the inorganic residue, and the driven-off balance will represent its organic fraction.

Total alkalinity, A_{tot} , is a measure of the total concentration of the OH^- , HCO_3^- , CO_3^{2-} , PO_4^{3-} , HSiO_3^- and SiO_3^{2-} anions and some salts of weak organic acids (humates) in a water sample. It is expressed in mmol litre^{-1} .

Since all of the above substances react with acids, the total alkalinity of a water sample is determined by the quantity of acid used for the titration of a water sample to the methyl orange end point. By far the most common constituents of alkalinity are bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), silicate (HSiO_3^-), hydroxide (OH^-), and phosphate (H_2PO_4^-),

Clarification mainly involves various forms of sedimentation in which case the impurities present in the water are caused to settle out as a sludge. These methods rely on the use of a range of agents which are added to the water. The sedimentation processes used to clarify water include coagulation, the lime process, and the magnesia process for silicon removal.

Coagulation is a physico-chemical process in which the colloidal particles present in the water stick together, or coalesce, upon contact, and the resultant flocs settle to the bottom of a water-treatment basin for subsequent discharge. The materials added to the water for the above purpose are referred to as *coagulants*. Those most commonly used are the sulphates of aluminium and iron, $\text{Al}_2(\text{SO}_4)_3$ and FeSO_4 .

The effect of coagulation can be enhanced by the addition of what are known as *flocculants* (such as polyacrylamide, activated silicic acid, etc.). Flocculants promote collisions between the suspended particles and thus speed up and improve floc formation.

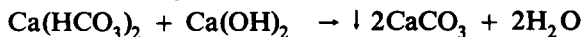
The *lime process* is used to remove bicarbonate alkalinity. At the same time, it reduces the hardness, salt content, suspended solids content, iron and silicic acid compound content of the water. In this process, slaked lime, $\text{Ca}(\text{OH})_2$ is added in the form of milk of lime. Removal of silicic acid is enhanced by the addition of caustic magnesite (70-80% MgO).

As a rule, the above operations are carried out all at the same time in a single vessel called the *clarifier*. Final removal of the sludge is effected by *filtration*. It may take place in the bulk of the filter medium (in which case it is known as adhesive filtration) or at the surface of the filter medium (in which case it is referred to as film filtration), depending on the relative size of the particles to be removed by filtration and the effective pore diameter.*

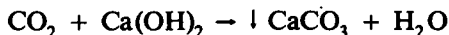
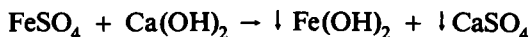
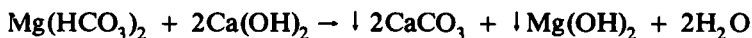
The most common filter media are quartz sand, crushed anthracite coal, sulphonated carbon, cellulose, perlite, volcanic slag, expanded clay, to name but a few.

Softening, or removal of hardness, is a process commonly practiced in water treatment to remove calcium and magnesium responsible for water hardness. Among the most effective processes is the *lime-soda process*, especially in combination with the *phosphate process*. The following chemical reactions are at the basis of softening.

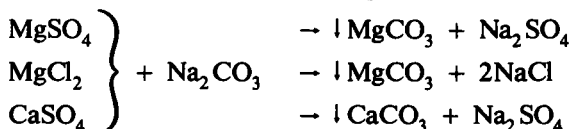
1. The addition of slaked lime to remove temporary hardness and iron ions and to fix the CO_2 :



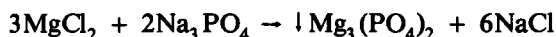
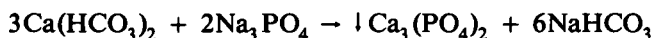
* In "*Chemical Engineers' Handbook*" by R. H. Perry and C. H. Chilton the two forms of filtration are termed 'filer-medium (blocking or depth) filtration' and 'cake filtration', respectively. — *Translator's note*.



2. The addition of soda ash to remove permanent hardness:



3. The addition of trisodium phosphate to promote the precipitation of Ca^{2+} and Mg^{2+} cations:



Since the phosphates of calcium and magnesium have a negligible solubility, the phosphate process is highly efficient.

Softening, demineralization and silicon removal can all be accomplished by *ion exchange* processes which are widely used at present. Ion exchange consists essentially in that the mobile hydrated ions of a solid, called an *ion exchanger*, are exchanged, equivalent for equivalent, for ions of like charge — positive or negative — in solution. *Cation exchange* occurs when the fixed charge groups of the exchanger are negative, and the solid is referred to as a *cation* (or *cationic*) *exchanger*. *Anion exchange* takes place when the fixed functional groups are positive, and the solid is referred to as an *anion* (or *anionic*) *exchanger*.

Cation exchangers are practically water-insoluble salts or acids. Their anion is responsible for insolubility in water, while their cation (sodium or hydrogen) can take part, under certain conditions, in an exchange reaction with the cations in solution. They are respectively called Na *cation exchangers* and H *cation exchangers*.

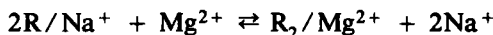
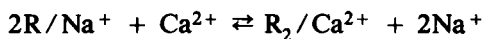
Anion exchangers are bases or salts with a solid, insoluble cation. Anion exchangers containing a mobile hydroxyl group are referred to as OH *anion exchangers*.

The most commonly used Na cation exchangers include the aluminosilicates glauconite, zeolite, and permutite. The most commonly H cation exchangers are sulphonated carbon and synthetic resins. The group of OH anion exchangers includes complex synthetic resins, such as urea resins.

Ion exchange between a solution and an exchanger is essentially a heterogeneous chemical reaction. Importantly, the impurities removed from water by ion exchange do not form a sludge and the process does not call for a continuous metering of the components.

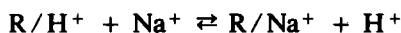
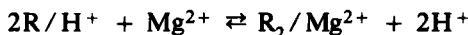
An important characteristic of ion exchangers is their *exchange capacity* — the ability to acquire a certain number of ions under specified conditions. The capacity of ion-exchange materials determines for how long the operating cycle of an ion-exchange filter can last. When a specified limit is reached, the ion-exchange material is subjected to regeneration — an ion exchange in the reverse direction.

The basis of water softening by cation exchange is the replacement of the calcium and magnesium ions, Ca^{2+} and Mg^{2+} , in the water with the sodium and hydrogen ions of the ion exchanger. The replacement involving sodium ions is referred to as *Na cation exchange*, and that involving hydrogen ions is termed *H cation exchange*:



where R/Na^+ stands for the solid matrix and the attached functional group without ion exchange. This complex is assumed to be univalent.

In the case of H cation exchange, the following reactions take place:



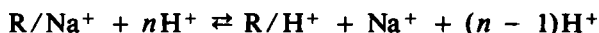
When the cation exchanger reaches a specified limit of exchange capacity, it is regenerated with a solution of NaCl or H_2SO_4 .

The regeneration of a cation exchanger with a solution of NaCl proceeds according to the scheme:

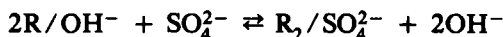
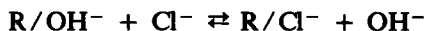


where $n - 2$ is the excess of NaCl over its stoichiometric quantity.

An H cation exchanger is regenerated with a 1—1.5% solution of sulphuric acid according to the scheme:



When the water is filtered through a bed of anion exchanger the anions are sorbed according to the scheme



Anion exchangers are usually regenerated with a 4% solution of NaOH

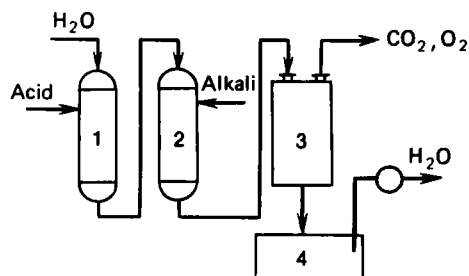


Fig. 11.2 Water softening unit:

1, cation exchange filter; 2, anion exchange filter; 3, deaerator; 4, water collector

according to the scheme:



Figure 11.2 shows a water softening unit which operates by using H cation exchange and OH anion exchange consecutively. When the water passes through a bed of cation exchange, it gets rid of its ions of calcium, magnesium in the H cation exchange filter, 1, then the anion exchange filter, 2, removes its anions. Following that, the water goes through the deaerator, 3, where it parts with its oxygen and carbon dioxide, flows through a collecting tank, 4, and finally goes to services. For regeneration, a sulphuric acid solution is fed to filter 1, and a solution of sodium hydroxide to filter 2.

An important step in water treatment is the removal of dissolved gases. Dissolved gases come about owing to their sorption and the chemical reaction that take place when impurities are formed in natural waters or in the water being treated at the various stages. These gases may be classed into those which do not react with water (H_2 , O_2 , and CH_4), and those which do react with it and with its impurities (NH_3 , CO_2 , and Cl_2). Also, they may be classed into corrosive (O_2 , CO_2 , NH_3 , Cl_2 , and H_2S) and inert (N_2 , H_2 , and CH_4). The concentration of gases in water is a function of many factors among which the leading ones are the physical nature of the gas, the degree of saturation, the pressure in the system, and the temperature of the water.

Dissolved gases are primarily removed from water by *desorption* (*thermal deaeration*). Basically, it consists in that the water is brought in contact with steam in which the partial pressure of the gas being removed is close to zero — this is a necessary condition for desorption to take place. This form of water treatment is mainly carried out in deaerators (or deaerating heaters) which may be of the vacuum, atmospheric, and

constant-pressure type. With regard to water distribution, the deaerators are classed into the spray type, the film type, and the bubble type. The working pressure range in vacuum deaerators is from 0.0075 to 0.05 MPa.

Sometimes dissolved gases are removed by chemical means. Chemical removal of oxygen, for example, consists in that strong reducers (known as *scavenging agents*) are added to water, such as sodium sulphite. Removal of H_2S is effected by chlorination.

Essentially pure water required for the manufacture of chemically pure reagents and drugs, for analytic and laboratory use may be obtained by demineralization effected by thermal evaporation of raw water and collection of the distillate. Thermal evaporation is mainly carried out in boiling-type evaporators, and the raw water is first softened by ion exchange.

11.4.3 Atmospheric Air

The terrestrial atmosphere is the gaseous envelope surrounding our home planet and extending out to an altitude of up to 2 000 km. It carries chemically free constituents unique in their properties, whose concentration steadily declines with altitude.

The total mass of the terrestrial atmosphere is estimated at 5.1×10^{15} tonnes, with 90% of the total being concentrated in the layer extending out to an altitude of 16 km.

The major, or permanent, constituents of the terrestrial atmosphere contribute varying amounts to the overall mass. In per cent by volume, the atmosphere's composition is this: nitrogen, 78.16; oxygen, 20.90; argon, 0.93; helium, neon, krypton, xenon and other inert gases, 0.01. For engineering purposes it is assumed that atmospheric air is 79% nitrogen and 21% oxygen.

In the chemical process industries, air is used mainly as a raw material and a reactant in chemical processes, and also as an energy source.

Pure oxygen separated by the fractionation of liquefied air is ordinarily used in the oxygen processes of metal making, in blast furnace practice, etc. Atmospheric oxygen is most often used as an oxidizer in the roasting of non-ferrous sulphide ores and of sulphur-bearing raw materials to obtain sulphur dioxide for the manufacture of sulphuric acid, pulp and paper; in the oxidation of methane in some natural gas conversion processes; in the incomplete oxidation of hydrocarbons to obtain alcohols, aldehydes, acids, etc. Nitrogen is utilized as a raw material in the manufacture of synthesized ammonia and other nitrogen-bearing substances, and also as an inert gas. In ammonia synthesis liquefied nitrogen is used to scrub the converted gas free of carbon monoxide, methane and argon.

Air is a commercial source for nearly all of the inert gases. One of the exceptions is helium which is mainly derived from natural gas where the helium percentage is higher than it is in atmospheric air.

The inert gases argon, helium, krypton, neon and xenon are gaining ever more ground as efficient protective media and working fluids in the production processes of chemistry, metallurgy, mechanical engineering, power generation, and other vital industries.

Air to be used as a reactant is given a special treatment according to the manufacture or process in which it will be utilized, so as to remove dust, moisture and contact poisons.

With regard to power generation, oxygen is above all used as an oxidizer to burn various fuels and produce thermal energy.

Air is also employed as a heat transfer or cooling agent in manufacturing and processing industries. Compressed air is widely used in various bubble-type mixers to agitate liquids and slurries, and in burner nozzles to atomize or spray liquids in reactors or furnaces.

11.5 Sources of Energy for the Chemical Process Industries

The chemical process industries to-day are among the biggest consumers of fuels and electricity; they widely use thermal, electric and mechanical power. At this writing, the breakdown of their energy requirements are as follows: electricity, 40%; thermal power (steam and hot water), 50%; and directly burned fuels, 10%.

High-temperature thermal energy (at above 623K) is mainly used to change the physico-chemical properties of raw materials or intermediates by firing or roasting, and also to step up the rate of reaction. This energy is derived by burning various fuels (coal, coke, blast-furnace and coke-oven gases, liquid fuels, and natural gas) directly in process equipment.

Medium-temperature (373-623K) and low-temperature (323-423K) thermal energy is utilized for process purposes in applications which entail changes in the physico-chemical properties of the source materials and require elevated temperature and pressure. These applications include pyrolysis (thermal decomposition), thermal cracking, evaporation, distillation, conversion, drying and heating in chemical processing, petroleum refining, wood processing and some other industries; the cleaning and sorting of raw materials (wet concentration of iron ores, washing in the chemical process, pulp and paper and light industries, etc.). Low-temperature thermal power is utilized to make work and life more comfortable, to supply hot water, heat, ventilation and air conditioning at factories, in public buildings, and in the homes.

Thermal energy for medium- and low-temperature processes mainly comes from steam and hot water. The long-term prospects are that their share in medium- and low-temperature thermal power will eventually rise to 80-85% of the total. More than 80% of the thermal power consumed by industrial chemistry is used up for process needs.

Electric energy is essential for electrochemical processes (electrolysis of solutions and melts) and electrothermal processes (heating, melting, sublimation, high-temperature syntheses, etc.). Industrial chemistry also uses processes which involve electromagnetic phenomena (in arc and induction furnaces, magnetic separation of materials, etc.) and electrostatic phenomena (electrostatic precipitation of dust and mist, electric cracking, etc.). Electronic, ionic and photoelectric phenomena are utilized for process control, monitoring and supervisory indication; electronics is especially widely used for chemical process automation. Electric energy also supplies light and mechanical power.

Mechanical power is mainly needed for physical operations, such as crushing, grinding, mixing, centrifuging, to drive pumps, compressors, fans and blowers, and also to carry out auxiliary operations (such as materials handling).

Of the bulk materials turned out by the chemical process industries, those most energy-intensive are ammonia, plastics, synthetic resins, methanol, caustic soda, soda ash, artificial fibres, calcium carbide, yellow phosphorus, sulphuric acid, synthetic rubber, and apatite concentrates. Their preparation or manufacture uses as much as 55% of the total electric and thermal energy and 95% of the total fuel.

The magnitude of utility (that is, steam, water, electricity, and fuels) requirements is greatly affected by the choice and preliminary preparation of the raw materials. For example, when ammonia is produced by the gasification of brown-coal semicoke, the energy consumption is 1780 kWh per tonne of nitrogen. With the gasification of heavy petroleum residuum, the figure is reduced to 1310 kWh per tonne of nitrogen. At present-day co-generation ammonia-producing plants which use natural gas as the source material and convert it with steam, the energy consumption may be brought down to a mere 60 kWh per tonne of nitrogen. Carefully prepared raw materials (with regard to their chemical composition, state of matter, and impurity content) will as a rule serve to bring down the utility requirements for the process as a whole.

In the Soviet Union, systematic work has always been carried out to extend the use of advanced chemical processes and better process designs. Still, there are reserves of fuel and energy savings. It is vital to put them to use as soon as possible because the chemical process industries rank second in terms of thermal energy consumption and third in terms of electric power consumption.

11.5.1 Classification of Fuel and Energy Sources

The major sources of energy used at present are fossil fuels (coal, petroleum, natural gas, peat, and shales), the products of their processing,

water, biomass (wood and other vegetable raw materials), and nuclear power. There is a limited contribution from the wind and the tides.

The world's reserves of the basic types of fuel are estimated at 12 800 thousand million tonnes of equivalent fuel. Of this quantity, about 11 200 thousand million tonnes comes as coal, 740 thousand million tonnes as petroleum, and 630 thousand million tonnes as natural gas.

The energy sources may be classed into *fuels* (coal, petroleum, natural gas, shales, bituminous sands, peat, biomass) and *non-fuels* (hydraulic energy, wind energy, solar radiant energy, geothermal energy, etc.). They may further be classed into renewable and non-renewable, primary and secondary.

All of the *renewable energy sources* are derivatives of solar energy. For convenience, however, they may be classed into the following categories:

- solar energy (direct radiation);
- hydraulic energy (the evaporation-condensation cycle);
- wind and wave energy;
- the biomass (of vegetable and animal origin).

The practically inexhaustible sources include geothermal and thermonuclear (nuclear fusion) energy. Geothermal energy may be utilized for heat supply and power generation. Nuclear fusion energy is measured in terms of the thermal equivalent of conversion of deuterium present in seawater and of lithium present in the Earth's crust.

The *non-renewable energy sources* include those whose reserves diminish irreversibly with mining. They include coal, shales, petroleum, bituminous sands, and natural gas.

All of the energy sources listed above fall in the category of *primary sources*. They contrast with the *secondary energy sources* which include the energy potential of the products, wastes, by-products, and intermediates of a given process plant. This potential is not utilized in the process plant itself, but may be reclaimed fully or in part to supply power for some other plant or pieces of equipment*.

The biggest suppliers of secondary energy sources are the chemical process, petroleum refining, petrochemical, iron and steel, non-ferrous, building-materials, gas, heavy machine-building and some other industries.

Secondary energy sources may be utilized directly without any change in the form of the energy-carrying medium so as to meet requirements in fuel and/or heat, or with some change in the energy-carrying medium so as to generate heat, electricity, refrigeration or mechanical work in waste-heat recovery units.

* Quite aptly, it is called *cogeneration power*. — *Translator's note*.

A fuel burned to generate electric power or heat at thermal power stations or district heating plants is referred to as a *power-generating fuel*. A fuel processed in various pieces of equipment (including industrial kilns and furnaces) to give various products and coke is classed as a *process fuel*.

Fuels may be solid, liquid, and gaseous. *Solid fuels* include brown and bituminous coals, anthracite coal, peat, shales, firewood, and products of their processing, such as coke, semicoke, peat and coal briquettes, heat-treated anthracite coal, and charcoal. *Liquid fuels* include petroleum, gas condensate and the products of their processing, such as gasoline, kerosene, Diesel fuel, residual oil fuel, tar and pitch, etc. *Gaseous fuels* include natural gas, casing-head (or associated petroleum) gas, mine gas, liquefied petroleum-refinery gas, coke-oven gas, semicoke-oven gas, producer gas, water gas, blast-furnace gas, cupola gas, hydrogen, and fermentation gases.

11.5.2 Technical Characteristics of Fuels

When burned, fuels supply power at thermal power stations, at factories, on vehicles, and in the homes. Many natural and man-made fuels are utilized as valuable source materials for the chemical process, petrochemical and allied industries.

The key technical characteristics of any fuel are its heat value (heat of combustion) and its maximum temperature of combustion.

The *heat value* of a fuel, or its *heat of combustion*, is the quantity of heat generated when 1 kg of solid or liquid fuel or 1 m³ of gaseous fuel is completely burned. It is expressed in kJ kg⁻¹ in the former case and in kJ m⁻³ in the latter. There may be the *low heat value*, Q_l^p , and the *high heat value*, Q_h^p . Here the superscript 'p' indicates that the heat value at constant pressure is meant. The low heat value refers to the quantity of heat generated when 1 kg of hydrogen is burned with the formation of water vapour. The high heat value refers to the quantity of heat generated when 1 kg of hydrogen is burned with the formation of water. Practical calculations ordinarily use the low heat value.

The *maximum temperature of combustion* refers to the highest temperature attained when a fuel sample is burned completely without an excess of air and when all of the heat thus generated is expended to heat the products of combustion. When calculating the maximum temperature of combustion, the fuel and air are assumed to be at zero temperature. The maximum temperature, $T_{\max}$, of a fuel is directly proportional to its heat of combustion and inversely proportional to the quantity of heat used up to raise the products of combustion to $T_{\max}$.

The maximum temperature of combustion is at the basis of fuel classification in terms of power generation. Thus, fuels are classed as high-

Table 11.1 Composition and Heat Values of Some Organic Fuels

Fuel	Per cent composition of combustible material, by mass				Heat value per unit of gross fuel*, kJ kg ⁻¹	
	C	H	S	O	high, Q_h^p	low, Q_l^p
Firewood	50	6	0.0	42	12000	10210
Peat (milled)	54-63	6	0.3	33	10330	8490
Shales	60-75	7-10	4.0	12-18	11550	11000
Brown coal:						
Moscow region	60-80	4-6	1-6	19-27	11840	10500
Kansk-Achinsk	70-72	5	0.3-0.8	23 max.	13390-17150	12550-14640
Anthracite coal	92-98	2	0.3-3	1-2	27610	27190
Bituminous coal:						
Kuznetsk	78-90	4-6	0.3-0.8	2-13	24270-28870	23850-28450
Donetsk	76-89	4.1-5.5	3-5	2-12	22170-27190	21760-26780
Ekibastuz	75-80	4.3-5.2	1.2-1.8	12-16	12550-19250	11710-18870
Natural gas	75	25	0.0**	0	39750 kJ m ⁻³	34730-35560 kJ m ⁻³
Gasoline	85	15	0.15	0	47280	43930
Low-sulphur residuum***	88 max.	11-12	0.5	0.02	43930	39750

* Gross fuel refers to the sum of its combustible material and ballast.

** The sulphur of natural gas from some deposits is mainly present as hydrogen sulphide.

*** Medium-sulphur residual fuel oil carries 0.5-2% S and the high-sulphur variety, 2-3.5% S.

temperature types if $T_{\max}$ is in excess of 2300K and as low-temperature types if $T_{\max}$ is less than 2300K. Those falling in the first group are natural, petroleum-refinery, casing-head, liquefied, water and semiwater gases, bituminous coal, coke, anthracite coal, semicoke, and charcoal. Those falling in the second group are firewood, peat, brown coal, shales, blast-furnace gas, producer gas, and the gas from underground coal gasification.

Any solid and liquid fuel consists of a combustible material and a ballast. The principal ballast constituents are moisture, nitrogen, the silicates, phosphates, sulphides and sulphates of calcium, iron, aluminium, potassium, sodium and other metals. The composition of the combustible component of a fuel and its ballast content have a direct bearing on its heat-generating and process qualities.

The major constituents of solid and liquid fuels are carbon (C), hydrogen (H), sulphur (S), oxygen (O), nitrogen (N), ash (A), and moisture (W). The constituents of gaseous fuels are various gases.

The sulphur of a fuel degrades its value and is a source of atmospheric pollution. In a solid fuel, sulphur may be present as sulphides, sulphates,

and organic compounds. When a fuel is burned, its sulphides and organic compounds are oxidized to form sulphur dioxide whereas the sulphate constituent passes into ash. In a liquid fuel, sulphur is present primarily as part of organic compounds, while in a gaseous fuel it is present as hydrogen sulphide, and partly as sulphur hydrocarbons and other compounds.

The most valuable hydrocarbon fuels, such as natural gas and light-weight liquid fuels (gasoline, etc.), have a combustible material consisting practically of only carbon and hydrogen and possess the highest heat value of all fuels.

The averaged composition and heat values of the combustible material of several organic fuels are given in Table 11.1.

11.5.3 Utilization of Secondary Energy Sources

In terms of the energy they can supply, secondary energy sources may be classed into three groups as follows.

(1) *Fuel (or combustible) secondary energy sources.* They comprise the chemical energy of wastes from the chemical and thermochemical processing of carbonaceous and/or hydrocarbon raw materials, combustible off-gases from blast furnaces, shaft furnaces, cupolas, converters, etc., the non-treatable wastes of lumbering and wood-working, evaporated combustible liquors, evaporated vinasse concentrates, bark and wood wastes from the pulp and paper industry, etc.

(2) *Thermal secondary energy sources.* They comprise the sensible heat of the off- or exit gases from process plant, in the products, by-products and intermediates of manufacturing processes, the working fluids of cooling systems, process plant, and in the hot water and steam spent in process and power equipment.

(3) *Positive-pressure secondary energy sources.* These comprise the potential energy of the gases and liquids leaving process plant at a pressure above atmospheric.

Secondary energy sources may be put to four uses, depending on the kind and parameters of the working fluids involved. These uses are as follows: (a) as fuels (in which case the combustible constituents are burned as fuels); (b) as sources of heat or refrigeration (which may be derived from the secondary sources directly or by waste-heat recovery or refrigerating units); (c) as sources of power (in which case the secondary energy sources are utilized in waste-heat recovery units to generate mechanical or electric power); (d) as sources of (a), (b) and (c).

Waste Heat Recovery Units. An important goal of process improvement in any industry is to tap as fully as possible all the likely secondary energy sources and to put them to industrial and domestic uses beneficial economically and ecologically.

As has been noted earlier, secondary energy sources may be utilized directly as fuels or converted to other forms of energy by waste heat recovery units. The choice of a pathway for the conversion of secondary energy sources depends on three factors: the quantity of secondary energy produced per unit time, the continuity of its availability, and its temperature level.

Heat can be reclaimed in processes that yield hot products and have at the same time cold streams which have to be preheated. This can be done in any one of several ways: by direct heat transfer through a heat-exchange surface or by means of extraneous heat-transfer agents.

Most often this job is done by waste-heat boilers which utilize high-temperature flue gases from industrial furnaces and chemical processing gases to generate water gas, by economizers which preheat boiler feed water, and by air heaters (of the recuperative or regenerative type) which function as traps to reclaim heat from high- and medium-temperature flue gases to supply hot air.

Secondary energy sources are also reclaimed in absorption and steam-ejector refrigerating machines, driers, and other pieces of plant.

Waste-heat boilers save a good deal of fuel as they generate power or process steam and supply hot water by reclaiming secondary (waste) heat. For example, the manufacture of sulphuric acid involves the burning of a sulphur-bearing raw material and the processing of the resultant sulphur dioxide into the acid. These operations generate a large quantity of heat: 7.1 million kJ per tonne of H_2SO_4 from pyrite, 5.77 million kJ from sulphur, and 8.03 million kJ from hydrogen sulphide.

The temperature of the exit gas leaving the furnace is 1073-1273 K.

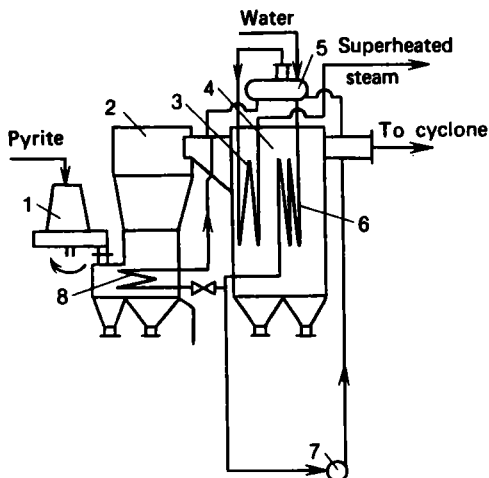


Fig. 11.3 Waste heat recovery unit:
1, feed bin; 2, fluidized-bed furnace;
3, steam superheater; 4, waste-heat
boiler; 5, drum separator; 6, cooler;
7, circulating pump; 8, cooler

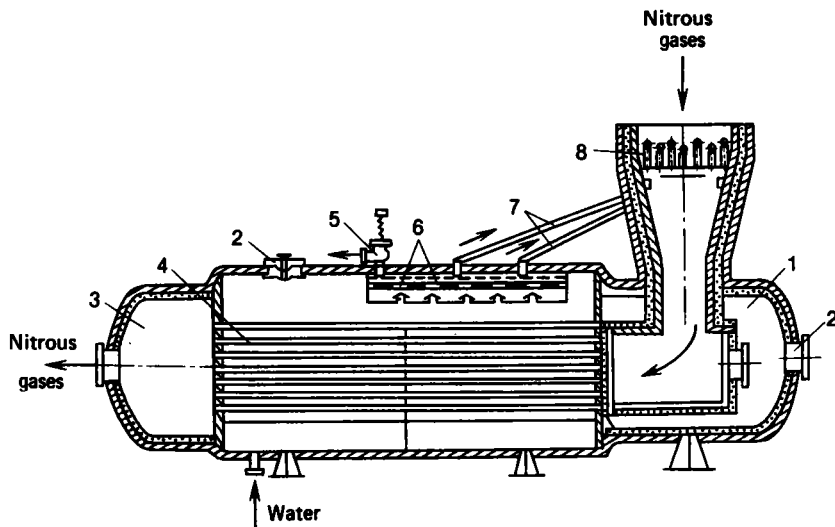


Fig. 11.4 Waste-heat boiler:

1, inlet chamber; 2, man-holes; 3, exit chamber; 4, evaporator tubes; 5, relief valve; 6, steam header; 7, saturated steam tubes; 8, steam superheater

An example of a very simple forced-circulation waste-heat recovery unit used in the manufacture of sulphuric acid is shown in Fig. 11.3. It has a drum separator, 5, which receives a steam-water emulsion from coolers 6 and 8. From the separator, the steam is routed to a steam superheater, 3, whence it is distributed to services at 703-723 K. The hot water collected by the separator is again routed by a circulating pump, 7, to the coolers. Before it enters the separator, water is purified, heated, and deaerated. This type of waste-heat recovery unit can generate as much as 1.5 tonnes of steam per tonne of pyrite burned by reclaiming the heat of reaction released in fluidized-bed furnaces.

Figure 11.4 shows the waste-heat boiler used in the manufacture of nitric acid from nitrous gases at a pressure of 0.68 MPa. The inlet chamber, 1, is topped by a cone enclosing the tubes of a superheater, 8. The cone attaches to the lower part of a contact vessel. The superheater operates in the nitrous gas zone at a temperature of 1153-1273 K.

The evaporating section of the boiler is a tubular heat exchanger, with nitrous gases passing through its tubes, 4. Water circulates in the inter-tubular space. The pressure of the water is about 1.27 MPa and that of the nitrous gases is 0.68 MPa. The wet gas is collected in a steam header, 6, routed over tubes, 7, to the superheater and leaves it at a temperature of 503 K. The boiler has man-holes, 2, and a relief valve, 5.

The manner in which the heat of reaction from ammonia synthesis is

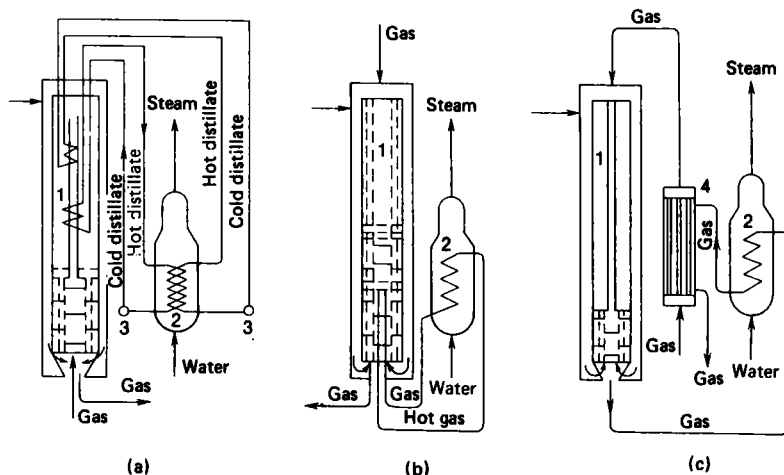


Fig. 11.5 Recovery of heat of reaction from ammonia synthesis:

a, two-circuit system; *b*, single-circuit system; *c*, single-circuit system; 1, vertical ammonia synthesis reactor; 2, waste-heat boilers; 3, circulating pumps; 4, external heat exchanger

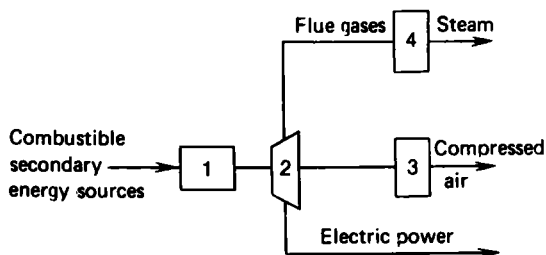


Fig. 11.6 Combustible secondary energy source reclamation system incorporating a gas turbine:

1, furnace box; 2, gas turbine; 3, air compressor; 4, steam generator

reclaimed with the aid of waste-heat boilers is illustrated in Fig. 11.5. By reclaiming the heat of reaction, this scheme generates 0.8-0.9 tonnes of steam per tonne of ammonia. The recovery of the heat of reaction substantially improves the economic and technical performance of ammonia synthesis reactors.

Contact economizers are employed to heat process and service water, to prepare boiler feed water, and also to supply the needs of air and low-temperature water heating and air conditioning. These units are called 'contact' for the reason that the flue gases are in direct contact with the water being heated. Contact economizers are able to cool flue gases to a very low level (down to 313 K) and to condensate as much as 70-80% of the water vapour present in the gas. They need a relatively small quantity of

metal for their construction, are simple in design, and are easy to operate and service.

Of special interest are systems which utilize secondary energy sources to generate electricity, steam and compressed air. An example of this type of cogeneration system is shown in Fig. 11.6.

Utilization of low-level secondary energy sources for refrigeration. It is advantageous to utilize secondary energy sources in absorption refrigerating machines to supply low-temperature cold for use in the chemical process, food, petrochemical and other industries and for air conditioning. The recovery of waste heat from the off-gases of furnaces and boilers, and from secondary steam and other secondary energy sources results in a substantial cut-down on the cost of refrigeration.

Absorption refrigerating machines depend for their operation on the absorption of refrigerant vapours by an absorbent (at the pressure of vaporization) and its subsequent separation (at the pressure of condensation) on heating. The most commonly used refrigerants are a water-ammonia solution, an aqueous solution of lithium bromide, and Freons. An absorption water-ammonia refrigerating machine is shown in block-diagram form in Fig. 11.7.

A concentrated water-ammonia solution carrying about 50% (by mass) ammonia enters a generator, 1, operating at an elevated pressure. The ammonia vapour thus generated is passed through a fractionating column, 2, and a reflux drum, 3, to leave them with an ammonia concentration of

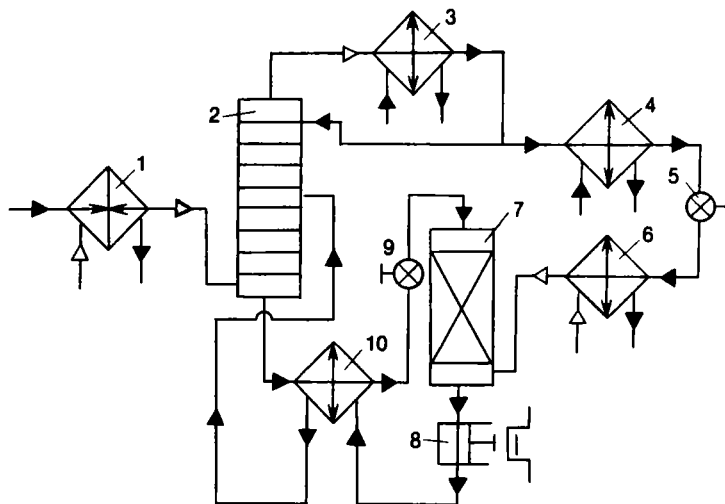


Fig. 11.7 Water-ammonia absorption refrigerating machine: 1, generator; 2, fractionating column; 3, reflux drum; 4, condenser; 5, throttle valve; 6, vaporizer; 7, absorber; 8, pump; 9, throttle valve; 10, heat exchanger

99.5-99.8% by mass. The vapour is then condensed by water cooling in a condenser, 4, the liquid ammonia is throttled down and admitted to a vaporizer, 6, where it evaporates and absorbs heat from the hot stream. The refrigerating capacity of the machine is the quantity of heat absorbed. From the vaporizer the ammonia vapour is routed to an absorber, 7, where it is absorbed by a spray of the weak (about 19.5%) water-ammonia solution fed from the fractionating column. The solution leaves the absorber with an ammonia content of about 32% and goes back to the rectifying column via a heat exchanger, 10, where the water-ammonia solution is raised in temperature by heat removed from the hot solution stream.

The performance of an absorption refrigerating machine is stated in terms of its *coefficient of performance for refrigeration*, or *cooling coefficient of performance*

$$\varepsilon_c = Q_c / Q_r$$

where:

Q_c = cooling (refrigerating or refrigeration) capacity of the machine

Q_r = quantity of heat transferred to the water-ammonia solution in the reboiler

Absorption lithium-bromide refrigerating machines are widely used to supply a refrigerant with a temperature of 278-288 K. The coolant is water, and the absorbent is a concentrated solution of lithium bromide.

11.6 Ways and Means of Improving the Effectiveness and Savings of Raw Materials, Fuels, and Energy

A better use and savings of raw materials, fuels and energy is a necessary condition for further advances in a country's economy. With special reference to the Soviet Union, the following approaches in handling this task may be outlined.

A very important approach is the use of natural resources in a rational and all-round manner and their saving through a wider resort to chemical, or man-made, materials, such as polymers, synthetic fibre, etc.

Another approach, now under way, is work on advanced electrochemical, plasma-chemical, membrane, photochemical, catalytic (with the use of macrocyclic compounds), biochemical, radiation (notably laser-beam), shock-wave and other processes.

Still another approach, practiced in many of the country's industries, is the industrial use of highly efficient power-generating and power-consuming plant, processes, and machines which provide for a high technical level of manufacturing and processing with minimal expenditures of material and energy resources.

An ever greater emphasis is placed on electric power and heat co-generation, and the development and use of MHD plants operating on gaseous and solid fuels.

Further impetus will be given to centralized heat supply from nuclear heat-and-power stations, nuclear heat generating stations, and large boiler houses. Energy can further be saved by improving the thermal insulation of plant and pipelines.

Plans are afoot to commercialize large co-generation plants and processes in the chemical process industries and autogenous processes in non-ferrous metallurgy.

A good deal is to be gained from the tonnage production of cement by the dry process, the use of plasma and electron-beam heating, and the secondary processing of petroleum as a way of increasing the production of light petroleum cuts.

The on-going modernization and replacement of existing and obsolescent power-generating and power-consuming equipment, the optimization of operating conditions for power-generating and process plant will go a long way towards cutting down the amount of raw materials, fuels, heat and electricity expended to turn out a unit weight of product.

The chemical process and other industries have set sights on a wider use of advanced control instrumentation to meter, monitor and optimize the consumption of fuel, heat and electricity by boiler plants, heat supply and electric power transmission systems.

Large quantities of raw materials and energy may be saved through a wider use of secondary material, fuel and energy sources, maximal recovery of heat from process plant, and recuperation of other forms of low-potential heat by means of heat pumps and absorption refrigerating machines.

There is quite a promise in the wide use of non-traditional (alternative) renewable energy sources, notable solar energy, geothermal energy, wind and tidal energy, and biomass.

The term 'biomass' refers to the renewable organic substance produced by plants via photosynthesis. The primary sources of biomass are trees, agricultural crops, and water plants. In terms of composition, biomass may be carbonaceous (such as vegetable materials, wood chips and sawdust, seawater algae, grain, paper, packaging materials) and sugar-bearing (sugar beet, sugar cane, sorgho). Biomass is a major renewable source of energy and may be utilized to produce hydrogen, gaseous, liquid and solid hydrocarbons, and chemical raw materials. Every year, the world's forests gain about 50 thousand million tonnes in weight, and photosynthesis yields 57×10^{15} tonnes of carbon a year — this is many times mankind's needs in energy.

In recent years, basic trends have been taking shape in the chemical and

biochemical transformation of the biomass into fuel and organic-synthesis products. National programs in this field have been launched in the United States, Great Britain, France, Brazil, Japan, Canada, China, Czechoslovakia, and many of the developing countries.

11.7 Cogeneration Technology — Its Importance and Essence

A most effective way to improve fuel consumption is cogeneration-based technology — recovery of all valuable constituents from a fuel and reclamation of the accompanying waste heat for power generation within the framework of a single processing unit.

Owing to cogeneration, the various operations that make up a given production scheme can be carried out at a higher rate, the fuel's heat and high temperature potential can be better utilized, and its organic and inorganic (ash) contents can be reclaimed to advantage and at a high energy efficiency*.

Cogeneration-based technology pursues two objectives. One is to devise ways and means for a better utilization of the organic and inorganic constituents of fuels burned for power generation at power stations and industrial plants. The other is to develop advanced energy-intensive cogeneration-based processes for the manufacture of pig iron, steel, nonferrous metals, building materials, chemicals, and other staple products using inexpensive fuels and configured to consume ever decreasing amounts of them per unit of product.

Thus, as is seen, cogeneration is closely related to an all-round utilization of fuel and stimulates the search for applicable processes.

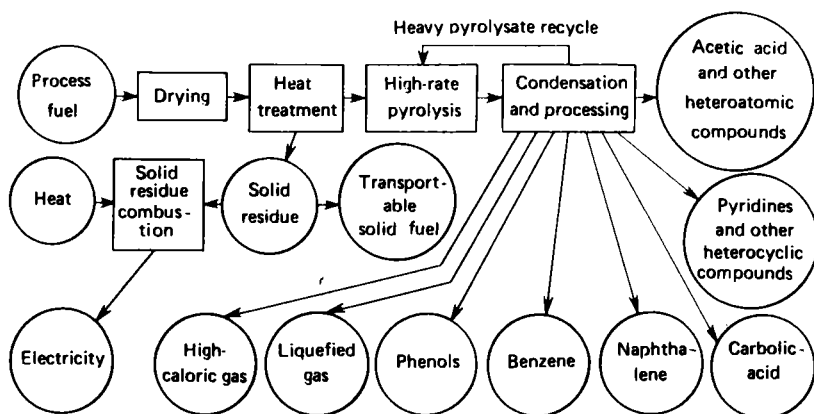
11.7.1 Cogeneration Technology as Applied to Fuels

The basic cogeneration scheme that improves the use of a fuel's constituents (which is the first objective that is sought by cogeneration technology) is what may be called the simple scheme. With it, a fuel before it is to be burned in a boiler furnace is subjected to a controlled heat treatment so as to derive a gas of high calorific value and valuable liquid products. The simple cogeneration scheme is applicable to most solid, liquid, and gaseous fuels, but the purpose it may serve will usually vary from one case to another. Simple cogeneration schemes for several fuels are described below.

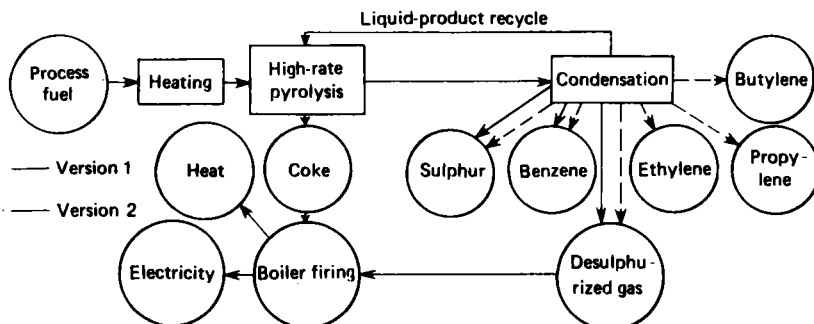
These simple schemes may be used to produce liquid resins and natural gasoline, both carrying valuable chemical raw materials; high-caloric gases containing the components of what is known as liquefied petroleum gas

* Here 'energy efficiency' is the ratio of usable heat to the total heat supplied by a fuel.

SOLID FUELS



HEAVY PETROLATUM RESIDUUM



NATURAL GAS

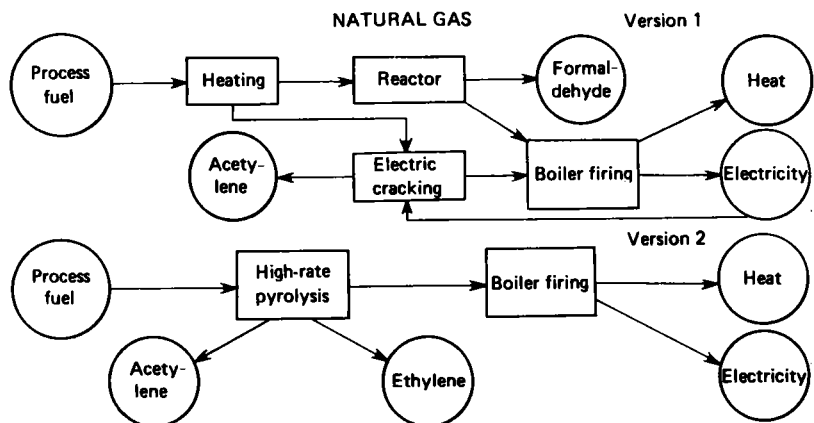


Fig. 11.8 Conversion of fuel to energy, gas and chemicals

(LPG) and the unsaturated hydrocarbons (olefins) ethylene, propylene and butylene; the rare and scattered elements germanium, tungsten, uranium, molybdenum, thorium, vanadium, titanium and some others; cement clinker and other building materials, such as slag felt, slag wool, and the like.

As applied to natural gas, cogeneration schemes provide for a high degree of processing with the production of gaseous sulphur, ethane, helium, and other valuable materials.

This combination of power generation and chemical processing permits a better utilization of the energy released by the chemical reactions, a more complete use of the utilities (electricity, steam and water), an improvement in product quality, and an increase in the throughput of plant.

11.7.2 Cogeneration Schemes Reclaiming the Heat of Reaction

In chemical processing today, special emphasis is placed on cogeneration-based processes and schemes which can reclaim the heat of reaction for power generation.

The best performance in this respect is shown by the tonnage manufacture of ammonia, weak nitric acid, and urea.

In ammonia synthesis, cogeneration has cut down the requirements in electric power to one-eighth (from 6840 to 900 MJ kg⁻¹). In urea manufacture, it has reduced the quantity of steam bought from outside suppliers by 40%; the capital costs have been cut down by 35-40%, and the manufacturing cost of the product has gone down by 10%. In the production of weak nitric acid, the consumption of electricity is now a fraction of its previous figure; on top of that over 5 GJ of thermal energy is generated and may be sold to other users.

Let us examine the principle underlying cogeneration process schemes, taking ammonia synthesis as an example. To make our discussion more instructive, we will first describe the generalized block diagram for ammonia synthesis (Fig. 11.9). It shows only the key steps in the process, and omits the specific plant items or units that would be necessary for a cogeneration scheme.

The first step is the catalytic steam reforming of methane in a tubular furnace-type reactor, or primary catalytic reformer, at an elevated temperature (800 °C). The second step is a combination of steam reforming and partial combustion of the residual methane with atmospheric oxygen in a shaft-type reactor called the catalytic combustor or secondary reformer, likewise at an elevated temperature (1000 °C). The third step is the CO shift conversion with steam at a temperature of around 450 °C in reactors called CO shift converters. The N₂ + H₂ mixture thus obtained is scrubbed free of its impurities in an absorber with an aqueous solution of

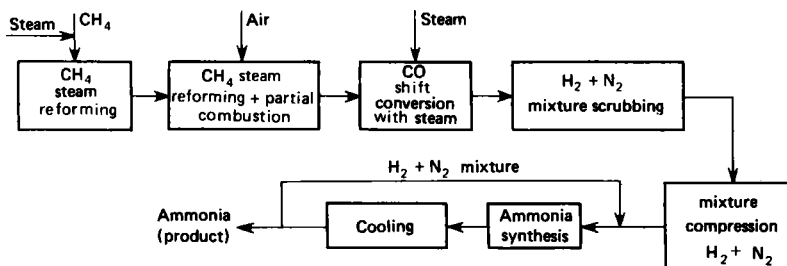


Fig. 11.9 Generalized block diagram of ammonia synthesis

monoethanolamine (this operation is effected at a pressure of 2.6 MPa), compressed in a compressor and routed to an ammonia synthesis reactor (the synthesis temperature is 400-500 °C).

The stream leaving the ammonia converter is cooled in a cooler, the product (ammonia) is separated, and the remaining H₂ + N₂ mixture is recycled to the ammonia converter for further synthesis.

Figure 11.10 shows the process flowsheet for ammonia synthesis combined with power cogeneration. The steam reforming of methane is effected in a primary reformer, 1, at an elevated temperature. To favour the reaction, the catalyst tubes are placed in a furnace fired with natural gas. Combustion gases have a high temperature, and their heat is reclaimed. To this end, the primary reformer has a convection chamber, 1a, where the passing hot flue gases give up their heat to

(a) the natural gas that comes in for steam reforming in the primary reformer;

(b) the air that is bled in for use in the further steam reforming and partial combustion in the shaft-type catalytic combustor or secondary reformer; and

(c) the steam that is used in the primary reformer for methane reforming and in the CO shift converter, 4, for CO shift.

After they have given up some of their heat, but still hot, the flue gases are routed to a waste-heat boiler, 11, to raise steam.

The streams leaving the secondary reformer and the CO shift converter also have a high temperature. In order to reclaim their heat, these streams are passed on to steam generators (waste-heat boilers, 3 and 5) where saturated steam is produced. It is then superheated in the convection chamber of the primary reformer and may be routed to one of the steam turbines (there are several of them in an ammonia synthesis plant). As shown in Fig. 11.10, steam is fed to a steam turbine, 8, mounted on a common shaft with a turbocompressor, 7, which compresses the H₂ + N₂ mixture entering the ammonia converter. In this way, less external energy is required to compress the gas mixture.

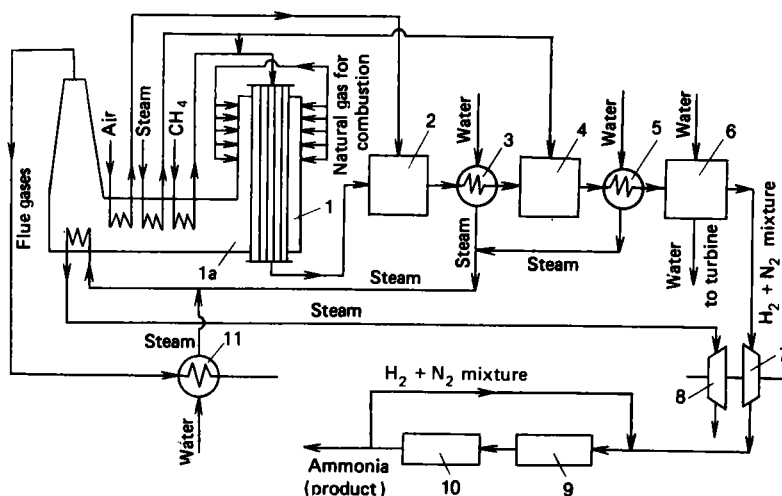


Fig. 11.10 Process flowsheet for ammonia synthesis with power cogeneration: 1, primary reformer; 1a, convection chamber; 2, shaft-type catalytic combustor; 3, waste-heat boiler; 4, CO shift converter; 5, waste-heat boiler; 6, absorber; 7, turbocompressor; 8, steam turbine; 9, ammonia converter; 10, heat exchanger; 11, waste heat boiler

An example of mechanical energy recuperation is given by the unit where CO_2 is removed from the $\text{H}_2 + \text{N}_2$ mixture. This is done in an absorber, 6, at a pressure of 2.6 MPa. The liquid leaving the absorber under pressure is fed to the water turbine mounted on a common shaft with the pump feeding water to the absorber.

11.7.3 Conversion of Brown Coal to Energy, Gas and Chemicals

Since its world reserves exceed more than 10-fold those of petroleum and more than 15-fold those of natural gas, coal ranks high as an energy source and a chemical raw material. Of special interest to the chemical process industries are brown coals which usually have a low calorific value.

Brown coals are low in ash (7-12%) and in sulphur (less than 1%) and are high in volatile matter (up to 48%). Unfortunately, their moisture content is high (30-40%) and their heat of combustion is low (12 550-15 900 kJ kg^{-1}). For this reason it does not pay to carry them in the 'as-mined' condition far away from the localities where they are mined. A far better way is to convert them to energy, gas and chemicals near or at the coal fields.

There is a program in the USSR which envisages three major applications for brown coals. They are proposed to be as follows.

(1) Tonnage heat treatment of brown coals in order to produce solid fuel, tar, pitch, gas, and tar-based synthetic liquid fuels for power generation, and their shipment to remote electric power plants.

(2) Use of the gases from the heat treatment of brown coals for the manufacture of ammonia, methanol, motor-fuel components, and fertilizers.

(3) Production of hydrogen and carbon monoxide for joint transport with electricity over a cryogenic superconducting line to distant users.

Referring to Fig. 11.11, the feed coal would arrive at a charring unit, 1, where it would be decomposed into char, tar, and volatile matter. The greater proportion of the char would be utilized as a clean-burning fuel to generate electric power (block 2), and the coarser fraction would be shipped by rail to remote users. The tar would be converted to synthetic liquid fuels for power generation (block 3), and the volatile matter in a vapour-gas state would be converted to synthesis gas (a mixture of hydrogen and carbon monoxide) in block 4. A fraction of the synthesis gas would be purified, liquefied and separated (block 5). The ortho-hydrogen would be converted to para-hydrogen by a catalytic process. Some of the synthesis gas and hydrogen thus produced would be used up near or at the coal field to process heavy residue into light motor fuel (block 6), to synthesize ammonia and urea (block 7) and methanol (block 8), and also for direct reduction of iron ore (block 9). The chemicals thus produced would be shipped by rail to remote users. Except for the fraction used up near or at the coal field, the electricity would be conveyed along with the liquefied hydrogen and carbon monoxide over a cryogenic, superconducting line (block 10). At the receiving end of the line the hydrogen would be treated for removal of deuterium (block 11). The superconducting line carrying the liquefied gas along with electricity can be built to handle large blocks of power and do the job of more than a dozen present-day power transmission lines.

When liquefied, hydrogen has a viscosity which is about one-fortieth of that of petroleum, so a pipeline a mere 0.5 m^2 in cross-sectional area would be able to handle 84.5 million m^3 of liquid hydrogen a year. With all of these factors taken together, the line could be built as a compact engineering structure.

Hydrogen and carbon monoxide, each a valuable energy source and raw material, can greatly enhance production when used in traditional manufactures and provide a basis for novel processes and power generation from hydrogen.

The extremely low temperature of liquid hydrogen and carbon monoxide could be utilized to liquefy air which could then be separated into oxygen and nitrogen (block 12). In this way, the electricity that is ordinarily used for the production of as much oxygen and nitrogen by traditional processes could be saved and a sizeable proportion of the energy used up to liquefy the gases at the coal field could be reclaimed in a deficient locality.

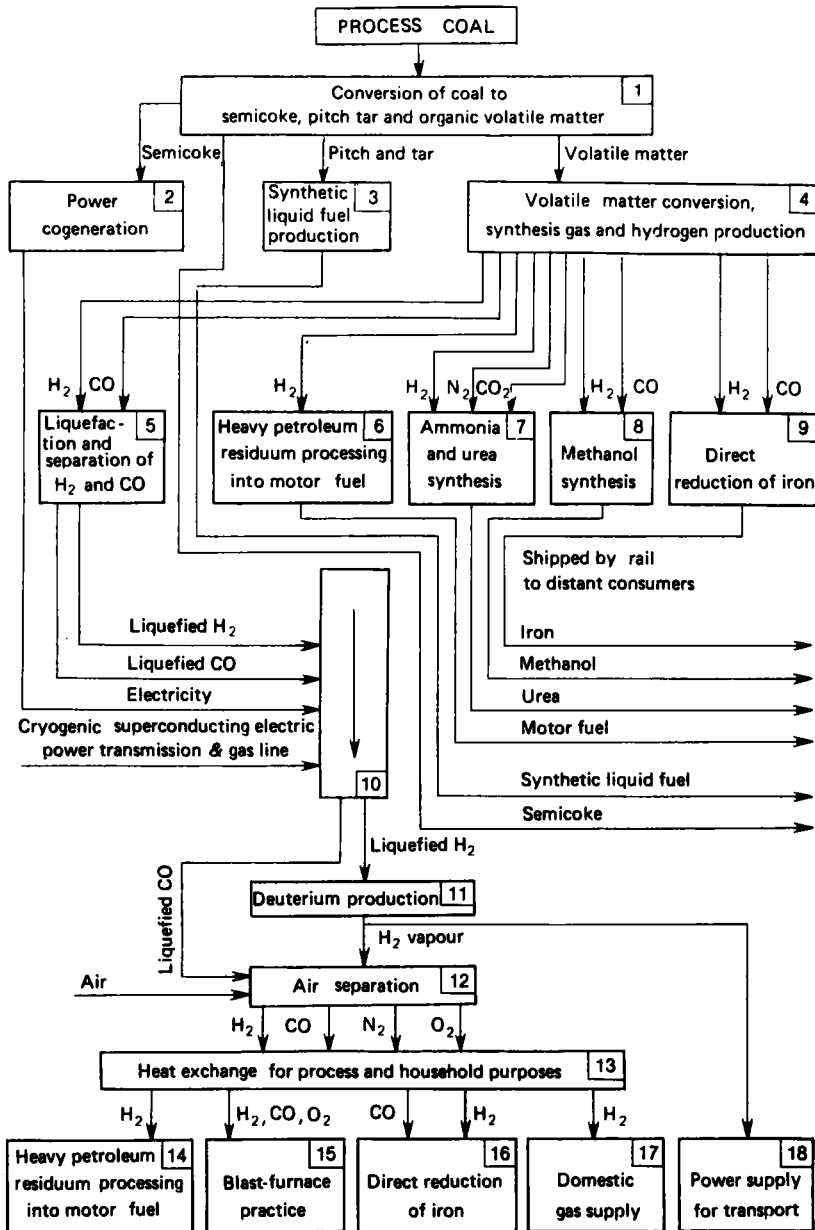


Fig. 11.11 Conversion of coal to energy, gas and chemicals

Some hydrogen could be used as a fuel for automobiles, air-craft, space vehicles, gas turbines and MHD-generators. The supply of liquid hydrogen carried as a fuel by vehicles would have a mass which is one-third to one-fourth of that of a traditional fuel — this would increase the payload and, in consequence, the range of aircraft (block 18) by a factor of 2.5.

The low-potential cold of the gases could be utilized in cold storage and refrigeration, to step up the rate of heat-transport processes, and as a basis for novel industrial cooling methods that would need no cooling water at all (block 13).

The nitrogen obtained by air separation could be used along with hydrogen and carbon monoxide to synthesize ammonia, urea and other fixed-nitrogen products whose production is in for an unlimited expansion in the future. This would save the natural gas ordinarily used for the purpose.

A mixture of 2 parts hydrogen and 1 part carbon monoxide could be utilized to synthesize methanol which could in turn be reprocessed into a wide range of chemical products.

Hydrogen could furthermore be used for the conversion of heavy petroleum residuum into light motor fuels and also for removal of sulphur from motor fuel (block 14). Some hydrogen would be used in gas supply to municipal services and the homes (block 17).

The oxygen disengaged from air through the use of the cryogenic temperature of liquefied gases could be used to step up the rate of blast-furnace, converter and other processes in ferrous and non-ferrous metallurgy (block 15).

Since they are ideal reducing gases, hydrogen and carbon monoxide could be used in blast furnaces and non-ferrous smelteries instead of natural gases presently blown into blast furnaces (block 15) and for the direct reduction of ores (block 16).

The conversion of brown coals to energy, gases, and chemical products we have just described is, of course, an ultimate program — its implementation will call for a good deal of scientific, research, development and engineering effort so as to work out new technologies and facilities, and all this will need a lot of money and a lot of time. In fact, it will be effected in a step-by-step fashion so as to reach the final goal in the specified time. At first a simplified version could be implemented, and this would later be perfected and expanded as more effective processes and facilities become available.

The final goal at any stage of the above program would be to utilize the fixed carbon of brown coals in the form of semicoke as a clean-burning fuel for power generation, and the volatile matter as a source material that could replace natural gas and crude petroleum in various manufactures.

11.7.4 Conversion of Coal into Energy and Chemicals at MHD Power Stations

As an example, we will describe the process based on the MHD generator developed by Krasnoyarsk University and the Institute of Theoretical and Applied Mechanics which is part of the Siberian Division of the USSR Academy of Sciences. This MHD-generator uses an unorthodox physical effect owing to which it can operate on the products of combustion without any readily ionizable agent added to the fuel. The process provides for cogeneration of electricity and recovery of valuable chemical products, notably methanol and motor fuel.

A detailed block diagram of the contemplated process is shown in Fig. 11.12. The working fluid of the MHD generator would be the carbon dioxide obtained by burning carbon monoxide in hot air. The CO_2 plasma leaving the MHD channel would be divided into two streams each of which would enter a cyclone gasifier. In the first stream the carbon dioxide would be reduced over semicoke to carbon monoxide, and molten slag would be separated. Then the CO stream would be routed through scrubbers, heat exchangers and a compressor to enter a combustor. Some of the CO stream would at the same time be utilized to preheat air and the main fuel stream in Cowper stoves.

There would be a second cyclone gasifier where the spent gas would be brought in contact with dried coal and steam to yield a $\text{CO} + \text{H}_2$ mixture (with a fraction of nitrogen) as a feedstock for the manufacture of chemical products.

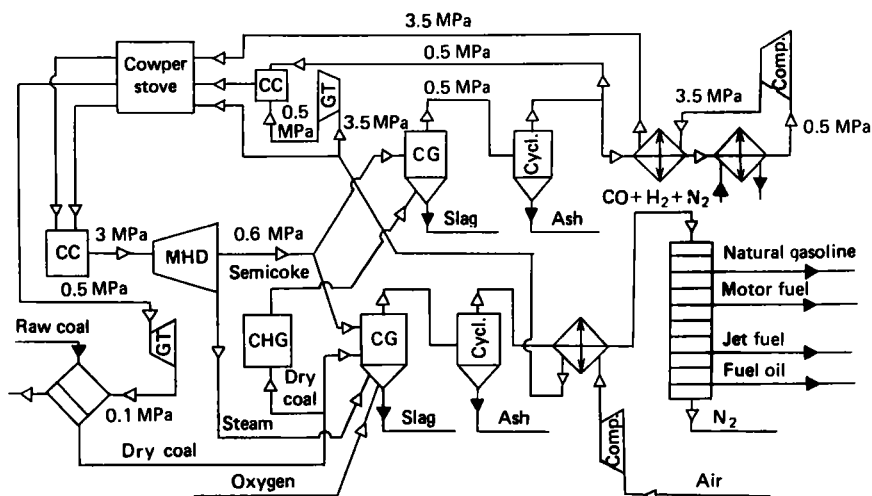


Fig. 11.12 Detailed block diagram of an MHD power station with chemicals coproduction: MHD, MHD generator; CG, cyclone gasifier; CC, combustion chamber; Cycl., cyclone; CHG, catalytic heat generator; Comp., compressor; GT, gas turbine

The preliminary preparation of coal would consist in drying it with off-gases, and the power-generating cycle would be extended to include pyrolysis in a catalytic heat generator to obtain semicoke.

The process would not include steam power-generating units — the excess pressure of spent gases is to be reclaimed in gas turbines.

11.7.5 Nuclear Power Stations as Producers of Energy and Chemical Products

Recent years have seen a growing interest in nuclear power stations that could simultaneously supply power and heat from their high-temperature nuclear reactors for energy-intensive processes, distribute heat to distant consumers, and support the manufacture of various chemical products.

For example, a nuclear reactor using helium at a temperature of 1223-1273 K may serve as a basis for cogeneration nuclear power stations which could support the manufacture of hydrogen, ammonia, synthesis gas, methanol, etc., and also stations supplying both electricity and heat for the chemical process, petrochemical, iron-and-steel and other industries. Their total output could well run into tens of GW (thermal). Plans to build nuclear power stations for long-distance heat supply and manoeuvrable nuclear plants based on high-temperature helium-cooled reactors and using helium regeneration could also add to the potentialities of this coolant.

From the view-point of the chemical process industries, special interest lies in the use of heat from high-temperature helium-cooled reactors in the tonnage production of ammonia and methanol.

A flowsheet for the coproduction of 3000 t/d of ammonia and 1020 t/d of methanol is shown in Fig. 11.13. Natural gas is subjected to catalytic steam reforming in a cascaded pressurized tubular furnace-type reformer, 4. Hydrogen is removed from the reformed gas by passing it through metal hydrogen-permeable membranes installed between the stages of the cascaded catalytic reformer. The high-purity hydrogen is mixed with the nitrogen removed from the exhaust gases of nitric acid manufacture and used as a feedstock for ammonia synthesis.

The $H_2 + N_2$ mixture is compressed to 32.0 MPa in a turbocompressor, 8, driven by a steam turbine, 9. The gases that have failed to pass through the 3rd permeable-membrane diffuser are used as a feedstock for the manufacture of methanol. On entering reactor 12, these gases undergo medium-temperature CO shift conversion following which the gas mixture is treated for removal of its hydrogen in the 4th diffuser.

The gases that have failed to pass through the 4th permeable membrane diffuser enter the 4th stage of the tubular reactor for the reforming of the residual methane. Removal of hydrogen and precise steam dosage prior to the methane reforming enable the reaction to proceed to a high degree

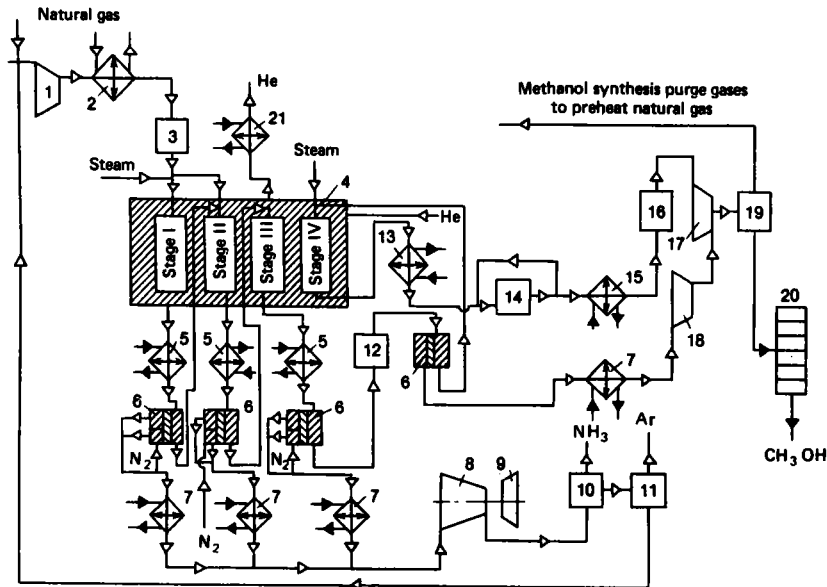


Fig. 11.13 Detailed block diagram of an integrated plant for the manufacture of ammonia and methanol and diffusion separation of hydrogen at the methane conversion step:

1, natural gas compressor; 2, preheater; 3, sulphur removal; 4, tubular furnace-type reformer; 5, waste-heat boiler; 6, diffuser; 7, waste-heat boiler; 8, turbocompressor; 9, turbine; 10, ammonia synthesis; 11, purge gas separation; 12, CO shift conversion; 13, waste-heat boiler; 14, CO shift conversion; 15, waste-heat boiler; 16, propylene-carbonate scrubbing; 17, compressor; 18, compressor; 19, methanol synthesis unit; 20, rectifying column; 21, waste-heat boiler

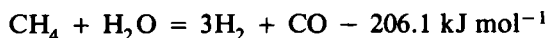
of conversion and to a low concentration of inert materials, notably the residual methane content of the feed gas used in methanol manufacture. The reformed gas leaving the 4th stage of the reformer is cooled to 723 K in a waste-heat boiler, 13, following which some of it is subjected to medium-temperature CO shift conversion.

The gas mixture is then subjected to propylene-carbonate scrubbing so that the CO₂ content of the feed gas is not over 6%. The hydrogen withdrawn from the 4th diffuser is compressed by a compressor, 18, and the gas mixture by another compressor, 17, to a pressure of 5.0-10.0 MPa. After mixing, they are routed to a methanol synthesis unit.

The purge gas from methanol synthesis is partly used as a fuel in the natural gas preheater and partly recycled to the catalytic reformer. The raw methanol is then enriched in a rectifying column, 20. The rectified methanol is used as product.

The required process steam at a pressure of 10.4 MPa is raised in a system of waste-heat boilers which reclaim the heat of the process gases, in

the heat-utilizing section of the catalytic reformer and in an additional boiler. The gas compressors of the ammonia and methanol sections are driven by condensing steam turbines. The oil and feedwater pumps of the steam boilers are driven by electric motors. The endothermic effect of the methane reforming operation



and the heat expended for power-generating and process needs are made up for by the heat of a high-temperature helium-cooled nuclear reactor.

The exergetic analysis of the above process has shown that the overall exergetic efficiency, η_{ex} , of the process is 0.757 when the helium coolant is maintained at a temperature of 2083 K. The figure is 0.823 at 1473 K, and 0.863 at 1223 K which is by 50% higher than in the traditional closed-cycle manufacture of ammonia and methanol.

In the petrochemical industry, the heat of a high-temperature nuclear reactor may be utilized to effect energy-intensive processes, such as cracking, pyrolysis, hydrofining, and reforming. In the nuclear-reactor petroleum processing complex shown in Fig. 11.14, for example, the heavy petroleum residue undergoes steam reforming in a reformer *C* at a temperature of 1073 K maintained by the heat of a high-temperature nuclear reactor *A*. Units *B* operating in the temperature range up to 825 K effect the primary and secondary processing of petroleum with the formation of motor fuels, heavy petroleum residues, and feedstocks for petrochemicals.

The flowsheet shown in Fig. 11.14 provides for a number of chemical processes and power cogeneration. The chemical processes yield fuels, hydrogen and other valuable products. In this way, effective use is made of both crude petroleum and the heat of a nuclear reactor.

High-temperature helium-cooled nuclear reactors may widely be used to effect radiation-chemical and thermal processes in the petrochemical industry. A unique opportunity in this respect is offered by high-temperature, gas-cooled nuclear reactors using spherical fuel elements. One of the uses for such units is irradiation pyrolysis for the manufacture of ethylene.

In coal technology, high-temperature helium-cooled reactors are convenient as sources of heat for the production of liquid and gaseous synthetic fuels.

Coal gasification by the heat from a nuclear reactor will cut down the manufacturing cost of synthetic liquid fuels by as much as 5 to 10% and will undoubtedly improve the economic and ecological performance of coal-processing plants.

Nuclear reactor complexes designed to generate power and to gasify coal for the manufacture of hydrogen, methane, and other secondary

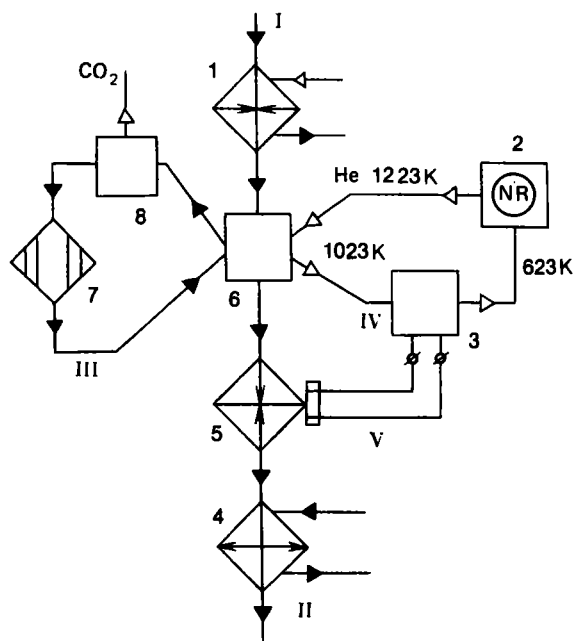


Fig. 11.16 Detailed block diagram for low-temperature dissociation of carbonates in special media (H_2 , H_2O) with reclamation of heat from high-temperature nuclear reactor:

I, feedstock preheater; 2, high-temperature nuclear reactor; 3, power-generating unit; 4, product cooler; 5, post-heat-treatment unit; 6, low-temperature dissociation unit; 7, dissociation medium regenerator; 8, separator; *I*, feedstock; *II*, product; *III*, dissociation medium; *IV*, helium; *V*, electric power

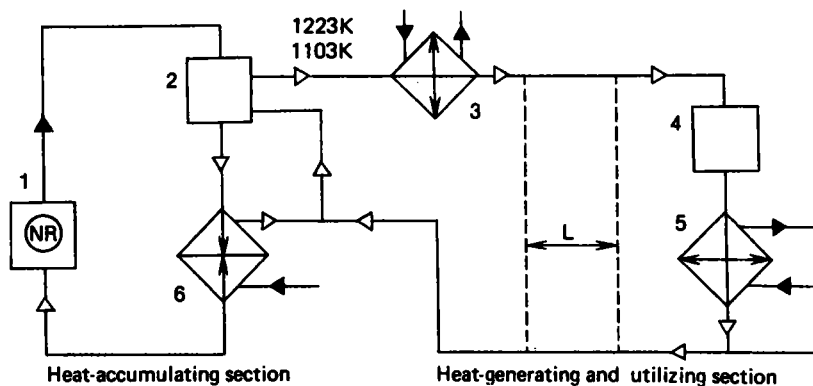


Fig. 11.17 Block diagram of a distant heat supply nuclear reactor-based chemothermal system:

1, high-temperature nuclear reactor; 2, methane reformer; 3, heat exchanger; 4, methanator;

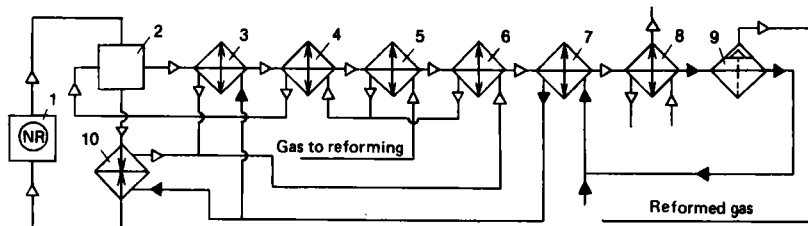


Fig. 11.18 Heat-accumulating section of a distant heat supply nuclear power station: 1, high-temperature nuclear reactor; 2, reformer; 3, 4, 5, 6, 7, heat exchangers; 8, air condenser; 9, separator; 10, heat exchanger

source in such a system could be a high-temperature nuclear reactor, 1. Its heat could be reclaimed to sustain the catalytic reforming of methane in a reformer, 2. The reformed gas consisting of hydrogen and carbon monoxide (synthesis gas) would be conveyed over gas lines to heat consumers where methanators, 4, would effect the catalytic synthesis of methane from the reformed gas with release of heat at 675-975 K.

After cooling the methane would be recycled back to the methanation step, and the remaining water could be used on the spot or likewise recycled to the methanation step.

As is seen from the flowsheet shown in Fig. 11.18, the heat accumulation section would include the catalytic steam reforming step effected with heat tapped from a high-temperature helium-cooled nuclear reactor, generation of process steam for reforming, preheating of the gas and gas-steam mixture coming in for the reforming operation, cooling of the gas, and condensation of the excess steam.

The mixture containing about 95% CH_4 , 1% CO_2 and 4% H_2 would be preheated in a heat exchanger, 5, to a temperature of 573 K by heat reclaimed from the reformed gas, and mixed in a specified ratio with superheated steam. The steam-gas mixture would then be heated in a heat exchanger, 4, to the kindling temperature (about 875 K) of the reaction and enter the catalytic reformer, 2. The process steam required for the reforming step could be raised partly by reclaiming the heat of the reformed gas in heat exchangers, 3 and 7, and partly by the heat reaching a heat exchanger, 10, from the nuclear reactor.

Figure 11.19 shows a flowsheet for methanation, heat generation and heat recovery. The upper temperature level of the heat generated in the methanators, 1, 4 and 6, may range from 675 K to 875-975 K, depending on the number of methanation stages used and the volume of recycled gas. At this temperature level it would be possible both to heat mains water or raise process steam in heat exchangers, 3, 5 and 7, and to generate power steam having the required temperature and pressure.

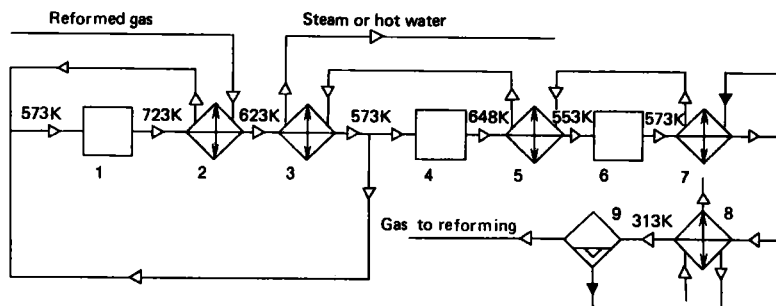


Fig. 11.19 Heat-generating and heat-consuming sections of a distant heat supply nuclear power plant:

1, methanator; 2, heat exchanger; 3, heat exchanger; 4, methanator; 5, heat exchanger; 6, methanator; 7, heat exchanger; 8, air condenser; 9, separator

Transport of heat in a chemically combined form offers a number of advantages over its transport as hot water. These advantages may be summed up as follows.

- (1) Less metal would be required for the heat transmission system per unit of heat conveyed.
- (2) No losses of heat would occur in transit.
- (3) The lines would need no thermal insulation.
- (4) The distance that could be spanned by such a heat transmission system may be greatly extended.

Long-distance heat-supply nuclear stations will materially expand the field of application for nuclear heat sources in industrial and municipal services so that a sizeable proportion of the scarce fuel gases and heavy petroleum residuum could be supplanted in the fuel and energy balances.

Chapter Twelve

CHEMICAL PROCESS INDUSTRIES AND ENVIRONMENTAL POLLUTION ABATEMENT

Protection of the environment and judicious use of natural resources in the setting of rapid advances in industry, transport and agriculture are primary concern to any nation.

A prominent place among the measures having as their objective to protect the environment is occupied by the advanced control of all emissions and wastes, and this includes their purification and recovery.

Recent years have seen a good deal of effort put into the development of water recirculation schemes, processes that leave little or no wastes at all, water treatment, dust removal and gas purification systems, and the utilization of solid, liquid and gaseous wastes as secondary raw materials.

The iron and steel, non-ferrous, nuclear, petrochemical, electronic and other industries widely use techniques of chemical engineering for the protection of biosphere.

12.1 Industrial Pollutants of the Biosphere

As is seen from Fig. 12.1, the industrial pollutants found in the biosphere may be classified into two general groups: material pollutants responsible for mechanical, chemical and biological pollution, and energy (or physical) pollutants.

Mechanical pollutants include aerosols, solid bodies and particles in water and soil. Chemical pollutants are various gas, liquid and solid chemical compounds which react with the biosphere. Biological pollutants are microorganisms and their wastes; this is an entirely new class of pollutants brought to life by the synthesis of yeast, actinomycetes, bacteria, fungi, and other microorganisms. Energy pollutants are related to all forms of energy, such as thermal or mechanical (vibration, noise, ultrasound), radiant (visible light, infra-red and ultra-violet rays), electromagnetic, ionizing (alpha, beta and gamma rays, X-rays, and neutrons), as left-overs from various processes. Some pollutants, such as radioactive wastes, belong to both material and energy groups.

The level of energy (physical) pollution is mainly brought down by shielding sources of noise, electromagnetic fields and ionizing radiations, by noise absorption, and vibration damping.

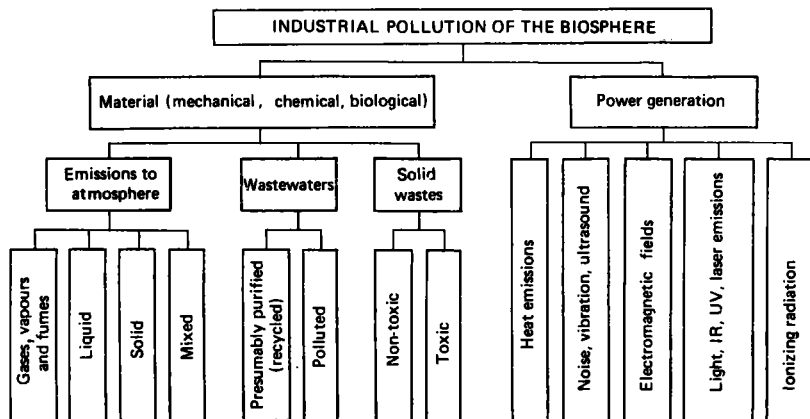


Fig. 12.1 Industrial pollutants of the biosphere

The sources of biosphere pollution may be classed into concentrated (point-type) and distributed, and also into those operating continuously or intermittently. Pollutants may further be divided into stable (nondegradable) and degradable under the action of chemical and biological processes.

12.2 Sources of Air Pollution

The atmosphere is polluted due to both natural processes and man's activity. Natural pollution comes from dust storms, volcanic activity, forest fires, droplet entrainment from the surface of the seas and oceans, etc. As a result, both solid and gaseous substances find their way into the atmosphere.

Dust lifted off the ground consists of fine particles of rock, soil, and remnants of plants and living organisms.

Volcanic eruptions liberate both gaseous substances which contain hydrogen chloride, hydrogen fluoride, ammonia, chlorine, carbon monoxide and dioxide, sulphur dioxide, hydrogen sulphide, water vapour, and also ash which mainly consists of silica particles.

Droplet entrainment from the surface of the seas and oceans leads to air pollution with the salts of calcium, magnesium, sodium, and potassium present in the seawater in dissolved state. As the droplets vaporize, the salts form tiny crystals which pollute the air.

In addition to particles of inorganic origin, the atmosphere contains varying quantities of minute microorganisms, fungi, bacteria, and spores.

Air pollution from natural sources is taken into account when determining the overall level of atmospheric contamination.

The principal man-made, or anthropogenic, sources of air pollution are emissions from large thermal power stations which burn solid, liquid or gaseous fuels, motor vehicles, iron-and-steel works, non-ferrous smelteries, and chemical complexes.*

The most typical emissions from iron-and-steel works and non-ferrous smelteries are dust, sulphur dioxide, nitrogen oxide, carbon monoxide, and hydrocarbons.

The emissions from chemical complexes carry substantially smaller quantities of contaminants, but unfortunately chemical plants are often situated in a close proximity to one another, and their emissions contain a number of extremely toxic compounds. This makes these contaminants

* Other authors give a wider range of anthropogenic contaminants. Thus, H.S. Peavy, D.R. Rowe and G. Tchobanoglous in their *Environmental Engineering* (McGraw-Hill Book Company, 1985) include aircraft, railroads, ships and the handling of gasoline, residential and industrial power and heating, pulp-and-paper industries, petroleum refineries, and solid-waste disposal. — *Translator's note.*

especially harmful, and many countries have national standards which set limits of maximum concentration for the substances discharged into the atmosphere.

According to state of matter, all air pollutants in gas emissions are classed into suspended solid particles (aerosols), such as dust and smoke, suspended liquid particles exemplified by spray and mist, and also gaseous and vapour forms.

The major air contaminants in terms of quantity are sulphur dioxide, carbon monoxide, nitrogen oxides, various hydrocarbons, and dust. They account for up to 85% of the total pollutants emitted into the atmosphere. For example, the combustion of an organic fuel draws large quantities of atmospheric oxygen and discharges carbon dioxide, water vapour, nitrogen, sulphur and other toxic compounds, and ash.

According to existing records, it took 1.3 thousand million tonnes of oxygen to burn all kinds of fuel in 1860; in 1960 the figure rose to 12 thousand million, and it may be expected that in the year 2000 it will rise to 57 thousand million. At this writing, the annual emission to the atmosphere with products of combustion the world over includes as much as 100 million tonnes of solids, about 150 million tonnes of sulphur dioxide, 300 million tonnes of carbon monoxide, and 50 million tonnes of nitrogen oxides.

The toxic emissions to the atmosphere from chemical complexes are organic solvents, amines, aldehydes, chlorine and its derivatives, nitrogen oxides, hydrocyanic acid, fluorine compounds, sulphur dioxide, phosphorus, mercury, hydrogen sulphide, carbon disulphide, organometallic compounds, etc. Sizeable amounts of toxic substances are emitted to the atmosphere in the manufacture of acids, alkalis, fertilizers, cement, soda, ammonia, synthetic fibres, dyes, pesticides, rubber products, organic solvents, etc.

A special group of air contaminants includes radioactive wastes discharged into the atmosphere mainly from nuclear and hydrogen weapon tests.

12.3 The Composition, Properties, and Classification of Wastewaters

Since chemical processing involves the use of a wide range of reactants, intermediates and products, its wastewaters are polluted with all kinds of organic and inorganic compounds. The key contaminants and their sources are listed below.

Pollutant source	Pollutant composition
Manufacture of mineral and inorganic salts	Inorganic acids, alkalis, salts (fluorides, sulphates, phosphates, etc)

Basic organic and petrochemical syntheses	Fatty acids, aromatic compounds, alcohols, aldehydes, etc.
Manufacture of synthetic resins, polymers, synthetic fibres, etc.	High-molecular-weight compounds, monomers, polymer fragments, etc.
Petroleum processing, thermal conversion of fuels	Petroleum products, lub and fuel oils, resins, surfactants, etc.

Wastewaters are extremely complex, multicomponent solutions which contain soluble and insoluble, reactive, toxic, flammable and explosive substances. As often as not, wastewaters may carry substances giving off a pungent smell (sulphides, disulphides, hydrogen disulphide, mercaptanes, etc.). The suspended material present in wastewaters may be capable of polymerization or scale formation, so it may be the cause of blockage in pipelines and headers. The surfactants carried in wastewaters may produce large quantities of foam.

Under the classification formulated by L.A. Kulsky of the Soviet Union, water contaminants are classed on the basis of their relation to the dispersion medium into four groups, each group having some common physico-chemical characteristics.

The first group of contaminants are water suspensions of insoluble substances varying in particle size from coarse to fine suspensions (10^{-4} - 10^{-5} cm and more).

The second group of contaminants are various hydrophylic and hydrophobic colloidal systems, high-molecular-weight substances, and detergents with particle sizes in the range 10^{-5} - 10^{-6} cm, capable of changing their state of matter according to the prevailing conditions.

The third group of contaminants are molecular aqueous solutions of gases and organic compounds whose particle size ranges from 10^{-6} to 10^{-7} cm.

The fourth group of contaminants are ionic solutions of electrolytes which dissociate in water and have a particle size of less than 10^{-7} cm.

Each group requires a special range of wastewater purification techniques.

Wastewaters widely vary in their phase and dispersion state and temperature. As widely varying are the modes of wastewater formation and discharge. In many industrial processes, wastewaters are collected and discharged intermittently rather than continuously.

Wastewaters from industrial chemical processes may be classed according to the origin and properties.

Reaction waters. These are typical of reactions which take place with the formation of water. They are polluted with both reactants and products. Their purification usually poses a serious problem.

Waters present in feedstocks. Free or fixed water is present in many raw materials (for example, coal, petroleum, and shales). In the course of

chemical processing, it is contaminated with various substances. For example, brown coal contains up to 40% moisture which is contaminated with phenols and other organic compounds during heat treatment.

Wash waters. Water is widely used in industrial chemical processes to wash both raw materials and products. Product quality often depends on how thoroughly the washing is done.

Liquors. They result when processing is done in aqueous media. For example, the suspension polymerization of styrene in an aqueous medium leaves wastewaters contaminated with styrene, polymer fragments, suspension stabilizers, etc. Crystallization from solution leaves liquors contaminated with mineral substances, and so on.

Water extracts and absorption fluids. When water is used as an extractive agent or an absorbent, solutions are produced which contain sizeable amounts of chemical substances. Especially large quantities of absorption fluids are formed in wet gas purification (in scrubbers, foam and other types of absorbers, etc.).

Cooling water. This is used at chemical plants to cool products and reaction vessels. Water not coming in direct contact with products is recycled, that is, put back into the process.

Further varieties of wastewaters result from vacuum pumps, stirred barometric condensers, ash sluicing, steam condensation, and the cleaning of plant, containers, rooms, etc.

The rain and snow falling within the premises of a chemical plant may also be contaminated with chemicals.

All wastewaters are removed from a chemical plant's site by closed sewers and conduits. To avoid mixing the wastewaters from different sources, it is customary to use a completely separated sewer system for each.

As a rule, the following grades of wastewater are handled as separate streams: those not contaminated in the course of processing (those left after plant cooling, some condensates, etc.); reactive waters (acid or alkaline); highly mineralized; contaminated with organic compounds; those containing components whose recovery is economically advantageous; those containing petroleum products and oils; those containing ill-smelling, highly toxic, flammable, or explosive impurities; rainwater; domestic wastewater; etc.

Large quantities of wastewater are re-used not only in chemical processing, but also in mechanical-engineering industries where it is utilized in many auxiliary operations, such as washing, degreasing, pickling, deposition of chemical, galvanic and paint coatings, as cooling fluid, as lubricant in rolling and stamping, etc. Wastewaters from mechanical-engineering works carry sizeable amounts of poorly decomposable surfactants,

phosphates, organic compounds (gasoline, trichloroethane, carbon tetrachloride, etc.), the salts of heavy metals, and other compounds.

Mechanical-engineering works also employ water recirculation systems as a way of reducing water usage and abating the pollution of water bodies and courses. Water re-use is effected with the aid of local water purification systems based on electrochemical, ion-exchange and other advanced methods of water treatment and component recovery.

12.4 Purification of Industrial Effluents

The method and the facilities to be used for industrial waste treatment depend on the composition, properties and concentration of contaminants and the desired degree of purification.

The degree of purification of a fluid (in %) is found by the equation

$$\eta = \frac{C_1 - C_2}{C_1} 100$$

where:

C_1 = contaminant concentration prior to purification

C_2 = contaminant concentration after purification

Wastes from chemical processing are widely treated by mechanical, chemical, physico-chemical, physical, biochemical, and thermal methods.

Mechanical methods depend for their effect on the difference in density between the dispersion and disperse phases, such as in sedimentation, or on the separation of the solid or liquid phase at or in a porous septum, such as in filtration. These methods are used to remove suspended solids from wastewaters and aerosols from waste gases.

The most important forms of sedimentation are as follows.

Sedimentation by gravity, or *settling*, is used to separate dusts, suspensions, and emulsions. Unfortunately, this method provides a low settling rate and fails to remove finely divided particles. It is mainly used for the partial separation of inhomogeneous mixtures.

Centrifugal sedimentation is the most effective method for the separation of dusts, suspensions, emulsions, and vapour (gas)-liquid systems. The required centrifugal force can be produced by rotating the inhomogeneous feedstock inside a stationary vessel (as in cyclones and hydrocyclones) or by rotating the impeller and the inhomogeneous feedstock together in a vessel (as in sedimentation centrifuges).

Filtration removes nearly all of the suspended particles from liquids and gases. There are two basic filtration mechanisms. In one, the filtered solids are stopped at the surface of the filtering medium and pile upon one another to form a cake of increasing thickness. This is known as *cake filtration*. In the other mechanism, the solids are trapped within the pores or body of the filtering medium. This is known as *filter-medium (blocking*

or *depth*) *filtration*. The driving force is the difference in pressure upstream and downstream of the filter. It can be supplied by feeding the stock under pressure (as in pressure filters), by applying a vacuum downstream of the septum (as in vacuum filters), or by applying centrifugal force across the septum (as in filtration centrifuges). Filter media may be cotton, woollen, glass, or synthetic cloth, wire nets, porous materials, ceramics, cermets, and particulate materials (such as coal, sand, gravel, diatomaceous earth, etc.). Submicron particles are removed from gas suspensions by fibrous filters using glass paper as the filter medium.

Chemical methods of wastewater treatment include neutralization of acids and alkalis, conversion of ions to poorly soluble compounds, coprecipitation of inorganic substances, oxidation, reduction, electrolysis, hydrolysis, and catalytic oxidation. These methods are mainly used to deactivate and remove the impurities of inorganic compounds.

Physico-chemical methods include flotation, extraction, electrochemical and sorption methods, fractionation (distillation and rectification), reverse osmosis, and some others. The sorption methods include absorption, adsorption, and ion exchange. Except absorption, the methods listed here are used to remove finely dispersed, colloidal and soluble substances from wastewaters.

Absorption and adsorption are widely used to remove toxic gases, fumes and vapours from gases.

Physical methods include precipitation in electrostatic or magnetic fields, acoustic coagulation, evaporation, and some others. The electric field is widely used in electrostatic precipitators to remove solids and liquids from gases. The magnetic field is employed for the selective recovery of ferromagnetic particles, iron-carrying slimes, and other materials possessing magnetic properties from suspensions. Acoustic coagulation occurs when a gas carrying dust, fumes or mist is irradiated with ultrasound. This causes the suspended particles to agglomerate, and speeds up their settling rate.

Biochemical methods are employed to purify sewage waters. They are based on the biochemical oxidation (biodegradation) of organic and some inorganic substances due to the life processes of microorganisms. Sewage water treatment uses two methods, one is *aerobic digestion* (*decomposition* or *decay*) in which there is a continuous inflow of atmospheric oxygen to the sewage water being treated. The other is *anaerobic digestion* (*decomposition* or *decay*) which proceeds in the absence of oxygen. Aerobic digestion is more versatile and more commonly used of the two. It provides for a maximum rate of biochemical oxidation and a maximum effectiveness in rendering the impurities inert and relatively pathogen-free.

Thermal methods are applied to solid, liquid and gaseous wastes and have as their objective to decompose the toxic organic substances present

with atmospheric oxygen at an elevated temperature so as to obtain non-toxic compounds. Industrial wastes are most often disposed of by incinerating them at a temperature of 1123-1253 K.

12.5 Purification of Waste Gases from Chemical Processing

The methods used to purify waste gases depend on the physico-chemical properties, state of matter, degree of dispersion, chemical composition, and concentration of the impurities.

Removal of aerosols. This is done mostly by mechanical and physical methods.

Mechanical methods may be classed into dry and wet processes. *Dry processes* include sedimentation by gravity, inertial sedimentation and centrifugal sedimentation in a wide range of settling chambers, louver-type dust catchers and cyclones, and filtration through cloth and fibrous filters.

Wet processes are versatile as they may be used to render a gas free of dust, fumes and mist. Basically they consist in that the gas to be cleaned is scrubbed with a liquid (water) in packed towers, dynamic spray scrubbers, foam dust catchers, Venturi scrubbers, and other types of gas cleaning plant. A very high efficiency in the removal of particles has been shown by film dust and fly-ash catchers, and by spray separation in tray-type and rectifying apparatus with two interfacial zones.

Physical methods are electrostatic precipitation and acoustical coagulation.

Electrostatic precipitation is based on the fact that the suspended particles of an aerosol injected into a high-voltage electric field acquire an electrostatic charge, move to one or the other of the grounded collecting electrodes between which the electric field is set up, and settle out there. Electrostatic precipitators are most effective and versatile of all gas cleaning equipment. Among their principal advantages are the capacity to handle large quantities of gas (millions of cubic metres per hour) at a relatively low hydrostatic resistance (60-250 Pa); a high degree of cleaning (90-99.95% purity); low power requirements (0.06-0.12 kW hr per 1000 m³ of clean gas); and ease of complete automation.

Electrostatic precipitators are widely used to remove solid and liquid particles from gases over a wide range of particle size. They may be operated at a temperature of 253-773 K under exposure to various corrosive media, with the gas being purified admitted at either superatmospheric or subatmospheric pressure.

Acoustical coagulation offers a means for speeding up the removal of finely dispersed dust and mist from gases. It consists in that the gas being purified is irradiated with ordinary or ultra sound, and this causes the fine aerosol particles (soot, sulphuric acid mist, fumes and smoke) to coalesce.

Removal of vapours and fumes. This can be done by using liquid absorption, solid adsorption, and catalytic oxidation.

Liquid absorption may use the selective solubility of impurities (physical absorption) or their chemical reaction with the active components of a liquid absorbent (chemisorption). Liquid absorption is used to remove sulphur dioxide, hydrogen sulphide, other sulphur-bearing compounds, nitrogen oxides, acid fumes (HCl, HF, and H_2SO_4), carbon monoxide and dioxide, various organic compounds (phenols, formaldehyde, volatile solvents, etc.) from gases.

The absorbents used for the purpose are water, ammonia solutions, alkali solutions, suspensions of calcium hydroxide, oxides of manganese and magnesium, magnesium sulphate, ethanolamines, oils, etc. Absorption purification is a cyclic operation — when the absorbent is exhausted, it is regenerated. In physical absorption, the absorbent is regenerated by heating and pressure reduction — this causes the absorbed impurities to desorb and increases their concentration. Most chemisorption operations are likewise reversible, so the chemisorbent may be regenerated.

The equipment used for absorption purification is similar to that used for wet aerosol removal.

Solid adsorption is based on the selective adsorption of components from vapour-gas mixtures by suitable particulate materials which have a large specific surface area. Adsorption purification may involve both physical adsorption and chemical adsorption (chemisorption). The adsorbents most commonly used are activated carbon, silica gel, alumina gel, natural and man-made zeolites ('molecular sieves').

The key requirements that industrial adsorbents are to meet are as follows: high adsorbing capacity, selectivity, thermal endurance, long service life without changes in the structure or surface properties, and ease of regeneration. Adsorption is mainly used to recover organic compounds, above all toxic ones, and also mercury vapour.

Gas cleaning by solid adsorption is effected in batch shelf-type reactors. Special promise is held by fluidized-bed adsorbers. Solid sorbents are regenerated by heating (so as to burn out the trapped organic material), and by passing a stream of superheated steam, air, or inert gas (nitrogen) through the sorbent.

Gas purification by catalytic methods is based on the reactions that take place in the presence of solid catalysts. As a result of these catalyzed reactions, the impurities present in the gas being purified are converted to ecologically safe compounds or to compounds readily removable from the gas.

Catalytic purification is used for the low-temperature oxidation of toxic organic compounds, carbon monoxide, nitrogen oxides, sulphur dioxide, hydrogen sulphide, and some others. When gases are purified over sorbent

catalysts, the process is known as *catalytic adsorption*. The catalytic methods make it possible to reclaim the heat of reaction, and this in turn provides for power cogeneration in addition to chemical processing.

Thermal methods are used to treat gas emissions carrying alcohols, ethers, esters, ketones, aliphatic and aromatic hydrocarbons, organic acids, and some other compounds when their recovery and recycling is impossible or not warranted. The treatment is effected in *thermal combustion* units (known as thermal incinerators or afterburners) at a temperature of 923-1173 K, the residence time of the gas in the reaction zone being 0.5-0.7 s. The throughput in terms of the purified gas stream is 2 to 25 thousand $\text{m}^3 \text{hr}^{-1}$, and the degree of purity may be as high as 95%.

When the concentration of combustible organic impurities is close to the lower combustion point, resort is made to *flare burning*, also known as *direct-flame combustion*. If the concentration of impurities is below the lower combustion point, the required quantity of heat is supplied by adding a supplemental fuel gas and by burning it in the gas stream being purified. The combustion gases are then passed through a waste heat recovery system to reclaim the waste heat and to reduce fuel requirements.

In some cases, use is made of *catalytic thermal combustion*. It is effected at a temperature of 533-813 K. This treatment leaves the treated gas more than 95% pure in terms of toxic constituents.

12.6 Basic Trends of Scientific and Technological Effort in Air Pollution Control

Advances in science and technology pose ever new problems before air pollution control.

An important task in this field is to develop better systems for complete removal of highly volatile solids varying in physico-chemical composition from waste gases and air with the subsequent utilization of the removed substances, and also systems intended to condense and reclaim organic substances so that they may be selectively separated and put back into the process or re-processed into marketable products. Another task is to improve the performance of equipment that deactivates and neutralizes toxic components in waste gases with the generation of heat or manufacture of marketable products.

Large-scale work is under way on processes and plant which could reduce to a minimum the emissions of processable gaseous, vapour and dust-like materials, and also processes for the condensation, recovery and conversion of low-concentration impurities from chemical waste gases in the presence of large quantities of dust and other materials. Novel processes are being developed for removal of impurities from waste gases with the aid of liquid absorbents which would cut down utility requirements and

absorbent consumption and provide for the separation of the recovered compounds for the subsequent re-processing into marketable products.

Emphasis is placed on the design of new types of high-performance equipment which could assure a maximum recovery of aerosols and gas cleaning, and reclaim heat from waste gases for industrial and municipal purposes. Air pollution control also envisages work on automatic process control systems which could optimize the use of air and gaseous raw materials and the operation of gas cleaning and dust catching equipment. Sizeable savings in energy and feedstocks could be assured from the use of closed-circuit air and gas recirculation systems.

Commercialization of new materials (catalysts, sorbents, filter media, etc.) will go a long way towards improving the purification of waste gases and the recovery of valuable components. As a further step, suitable processes could be developed for the regeneration and re-work of these materials into marketable products at the end of service life or in case of failure.

Studies are being carried on so as to assess the usability of novel physico-chemical processes based on fundamental research for the purification of waste gases and air.

12.7 Treatment of Wastewaters from Chemical Processing

Wastewaters from chemical processing are treated by mechanical, physico-chemical, biochemical, and thermal methods. A general outline of these methods is given in Sec. 12.4. Here we will classify the basic methods according to the phase and dispersity characteristics and chemical composition of the impurities.

The choice of a wastewater treatment scheme depends on many factors. Above all, it should keep to a minimum the discharge of final effluents into water bodies and courses, provide for a maximum re-use of purified wastewaters in industrial processes and in water recirculation systems, and assure a more complete recovery of valuable impurities.

As is customary in the USSR, the wastewater treatment equipment may be classed into three major groups: local (within a processing unit), general (for a chemical complex as a whole), and district or community. The chemical process industries mostly use local and general wastewater treatment facilities. District or community facilities are intended, as their name implies, to handle the sanitary-sewage and industrial wastewaters of a given district or community.

Mechanical methods mainly include settling, clarification, and filtration. Their objective is to remove coarse suspended particles.

Physico-chemical methods are employed to remove finely dispersed, colloidal and dissolved substances from wastewaters. They include flota-

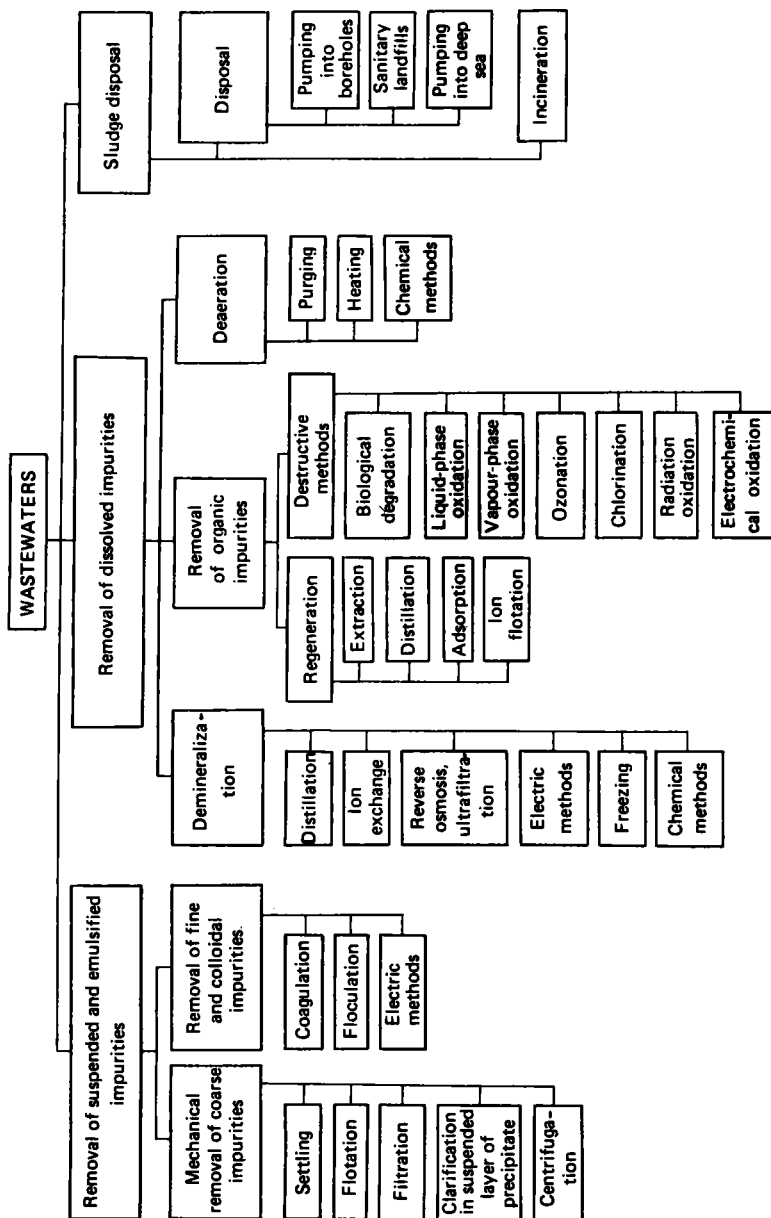


Fig. 12.2 Basic methods for wastewater treatment

tion, distillation, rectification, absorption, ion exchange, reverse osmosis, and some others.

Flotation is widely used to clarify wastewaters polluted by light-weight and highly dispersed suspensions. Flotation consists in that the suspended particles attach themselves to the air bubbles dispersed in the suspension and float together to the surface to form a froth. In addition to the solids, the froth also collects many emulsions and various surfactants dissolved in the wastewater.

Finely dispersed and colloidal particles and low-concentration emulsions are removed with the aid of *coagulants* and *flocculants*. The most commonly used coagulants are $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 which may be employed separately or as a mixture. In the latter case, the coagulation can occur over a wider range of pH values and temperatures. The effect of coagulation is boosted by the addition of flocculants (polyacrylamine, activated silicic acid, and some others). The flocculants speed up the formation of flocs, improve their structure, and enhance the efficiency of water clarification.

Soluble inorganic compounds are removed from wastewaters by means of *ion processes*, such as the conversion of the impurities into slightly dissociated compounds (by way of neutralization and complex formation), the fixation of anions and cations on a solid substrate (H and Na cation exchange and OH anion exchange), separation through a change in the phase state of the water by turning it to a vapour (distillation) or to a solid (freezing-out, hydration), re-distribution of ions in the liquid phase (extraction, reverse osmosis), ion separation in an electric field, etc. Most often, the equipment that effects these operations supplements the main wastewater treatment plant.

The gases and molecular-soluble organic substances dissolved in wastewaters are removed with activated carbon. For its effect activated carbon depends on the fact that the water-dissolved impurities enter into a molecular interaction with the carbon and attach themselves more or less firmly to its highly extended surface. Activated carbon is a good collector of compounds which are only slightly soluble in water.

Biochemical methods are applied to wastewaters that carry organic substances in the dissolved or finely dispersed state. Some microorganisms can digest even the inorganic compounds of carbon, nitrogen, phosphorus, potassium and other elements.

Biochemical treatment may be effected as aerobic digestion or anaerobic digestion. Of the two, aerobic digestion is used more often. Anaerobic digestion is mainly employed to ferment the sludge and, sometimes, to denitrify wastewaters.

During the biochemical treatment of wastewaters, some substances degraded by microorganisms take part in biosynthesis (the growth of

biomass, that is, activated sludge or the biofilm), and others are turned into safe products of oxidation, such as water, CO_2 , N_2 , etc.

The wastewater treatment facilities utilizing biochemical processes may be classed into two groups: facilities in which wastewater treatment proceeds under conditions close to natural (sewage farms, ponds and lagoons) and facilities in which wastewater treatment takes place under artificial conditions (biofilters, aeration tanks, aeration filters, and methane digesters).

On the demerit side of the biochemical methods are high capital costs, low oxidation rate (which has to be made up for by an increase in the volume of wastewater treatment facilities), high sensitivity to changes in temperature and impurity concentration, and toxicity of some organic and inorganic compounds with regard to microorganisms. For example, phenol, formaldehyde, ethers, esters, and ketones denature the protein of the protoplasm or destroy cells. Toxicity is especially high in the case of the salts of heavy metals (Hg, Sb, Pb, Cr, Cd, Co, Ni, Zn, Cu, and Fe) and some inorganic salts present in wastewaters in large quantities.

Some compounds typical of chemical processing (nitrobenzene, dichloromethane, DDT, 1,2-dichloroethane, chloroform, chlorobenzene, tertiary alkylbenzene sulphonates, ethyl ether, cyclohexane, hydroquinone, and some others) are not practically degradable by microorganisms.

The dissolved organic compounds can be removed from wastewaters by regenerative methods (distillation, extraction, adsorption, rectification, ion exchange, reverse osmosis and ultrafiltration, flotation, etc.) and by destructive methods (flame deactivation, liquid-phase oxidation, thermocatalytic oxidation in the vapour phase, and ozonation).

Apart from the deactivation of wastewaters, the regenerative methods recover valuable impurities from the water. These methods gain in importance and hold out special promise in connection with wasteless manufacturing and processing.

The destructive methods are used when it is impossible or economically unwarranted to recover the impurities from wastewaters.

The bacterial pollutants of wastewaters are destroyed by disinfection.

12.8 Water Recirculation Systems

Closed-circuit water recirculation systems used as part of individual processes, plants, or industrial complexes are a major approach to the rational use and conservation of water resources. In a closed-circuit system, the required amount of water is made to circulate and be re-used without any discharge of wastes to external water bodies or courses, and the amount of fresh water is limited solely to what has to be supplied in order

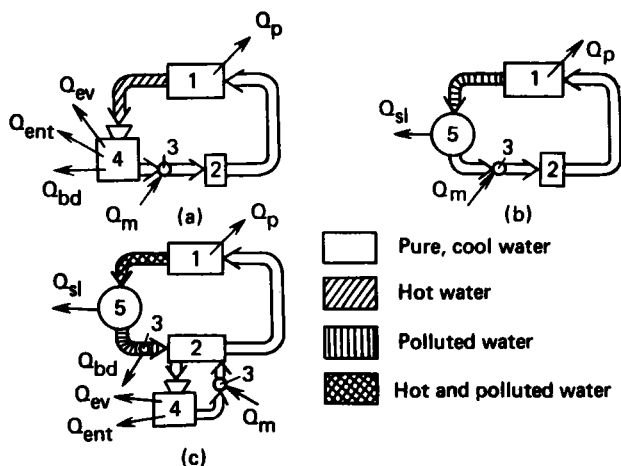


Fig. 12.3 Water recirculation systems:

a, recirculated water cooled; *b*, recirculated water purified; *c*, recirculated water both cooled and purified; 1, plant; 2, pump station; 3, chamber; 4, cooling tower; 5, water treatment facilities; water losses: Q_p , process; Q_{ev} , with evaporation in cooling; Q_{ent} , entrainment from cooler; Q_{purge} , discharge from system following a purge; Q_{sl} , with sludge; Q_{mu} , make-up

to make up for the losses through evaporation, water drop entrainment, and other natural causes.

At present, three basic versions of water recirculation schemes are in use (Fig. 12.3). With version 1, the water is only heated. With version 2, it is only polluted. With version 3, it may be both heated and polluted. In version 1, it is cooled in a water cooling tower or some other cooling facility (Fig. 12.3*a*). In version 2, the water has only to be purified (Fig. 12.3*b*). In version 3, it has to be both purified and cooled (Fig. 12.3*c*). Following that, the water is recycled back for re-use.

Thus recirculated around a closed loop, the water re-used many times is heated, cooled, partly evaporated, aerated, picks up salts, may become less stable, more corrosive and capable of forming deposits of mineral salts and bacterial growth. The quality standards for recirculated water are formulated for each particular process. Most often, closed-circuit water recirculation systems are used for cooling. Recirculation systems supplying purified water for process purposes are being used on a limited scale as yet. Examples are the manufacture of acetylene and ammonia, petrochemicals, gasification of shales and brown coal.

The effectiveness of an industrial water recirculation system may be expressed in terms of the water utilization ratio

$$K = (Q_f - Q_d)/Q_f$$

where:

Q_f = quantity of fresh water withdrawn from a supply source
 Q_d = quantity of water discharged to a wastewater pond or lagoon

Wide use of water recirculation systems in chemical processing, the change-over from water to air cooling, and improvement in manufacturing processes are major approaches to a reduced water consumption in the chemical process industries. In the USSR, these measures have served to cut down water use substantially in a number of basic chemical industries. For example, the water requirements have been brought down from 10 to 0.3 m³ per tonne of weak nitric acid, from 5.3 to 3.1 m³ per tonne of sulphuric acid, and from 77 to 3 m³ per tonne of wet-process phosphoric acid.

The number of cycles that re-used water may be put through can be enhanced by comprehensive pre-treatment, including removal of suspended matter and reagent treatment with a view to reducing its corrosiveness and suppression of bacterial growth. When suitably treated, wastewater may also be put back to use.

12.9 Basic Trends of Scientific and Technological Effort in Water Pollution Control

Water pollution control is gaining in importance all the time. One of the major fields of activity here is to improve systems for the selective separation of valuable components from wastewaters so that they can be made into marketable products and the water may be re-used. These systems use sorption-extraction processes for wastewater treatment based on various physico-chemical principles. Work is under way on new sorbents and extractive agents for the selective removal of impurities from wastewaters, and on processes for their production, regeneration, and re-work.

The methods used to separate valuable components from wastewaters in a form suitable for the subsequent manufacture of marketable products include sedimentation, crystallization, evaporation, distillation, combustion, etc.

Better systems are being built for the biological treatment of wastewaters from chemical processing, more items are being added to the list of substances that can be degraded to a neutral state by micro-organisms, and an ever wider use is being made of the resultant sludge reprocessed into marketable products or used to generate power.

In the chemical process industries water is saved through the use of recirculation systems adapted to the needs of each industry and optimized

in terms of development and operating costs, and also by processing raw materials and intermediates so as to minimize water use or to replace water with some other solvents (provided there is an effective system for their recovery and regeneration) and to do away with water completely. Developmental work on processes is accompanied by that on plant which would keep water use to a minimum. The new materials used in some equipment will also serve this purpose.

More local wastewater treatment systems are being built for recovery of valuable components from the effluents. Multipurpose water recirculation systems are being set up at chemical complexes.

The reclamation of heat from wastewaters for industrial and other uses will save a good deal of fuel and power. Automatic process control systems can meter water in the amounts precisely needed for the normal operation of chemical process plant.

12.10 Wasteless Chemical Processing

Purification of waste gases and waters is an emergency measure dictated by imperfections in industrial processes. Of course, water and gas purification prevents the discharge of objectionable substances into the biosphere, on the one hand, and reclaims these substances as concentrated solid wastes on the other. Still, the solid wastes that have not been used and are therefore dumped will pollute the environment all the same.

One way to reduce the quantity of such wastes substantially, to minimize their detrimental effect on the environment, or to convert them to compounds amenable to re-work is to set up wasteless chemical processing.*

The development of wasteless chemical processes and the associated wasteless chemical industries is one of the most urgent tasks facing chemical engineering. This is a socio-economic task of important significance — its achievement will raise the economic level and industrial potential and provide for an optimal ecological interaction between industry and the environment.

Wasteless chemical processing envisages the use of optimal process layouts with closed-loop material and energy flows. Ideally, there should be no waste waters, objectionable emissions to the atmosphere, or solid wastes.

* 'Wasteless chemical processing' is a relative term because we will never, in actual conditions, do away with all wastes or with the effects of industry on the environment. More accurately, this is 'low-waste processing' in which effluents and emissions are kept to a minimum so that the self-purifying ability of Nature could be sufficient to prevent irreversible ecological changes.

Work on wasteless chemical processing is going on in several directions. Among other things, processes are being developed in which the water consumption per unit of product is kept to a minimum, toxic starting materials are replaced with non-toxic ones, and volatile solvents are excluded from the process. Also, the quantity of wastes is minimized through the use of larger pieces of process plant, conversion of raw materials to chemical products and co-generated energy, and better methods for the treatment of wastewaters and gas emissions. Wasteless chemical processing provides for the highest achievable utilization of raw materials and energy owing to the better selectivity of the processes, recovery and reclamation of by-products and wastes, and better plant and methods for the local purification of the material streams before they are recycled or reclaimed. In some cases, wastes can completely be done away with through the maximum use of recirculated water and elimination of effluents. A good deal of effort is being put into the development of schemes for the all-round processing of raw materials with a maximal recovery of valuable products.

The chemical, petrochemical and other process industries in the USSR are carrying out a broad gamut of measures which have as their objective to modernize their respective technologies, to integrate closed-circuit water usage and air cooling into practice, to overhaul obsolescent and obsolete processing units, to encourage a wider use of wastes, and to achieve, in the long run, truly wasteless processing.

Among other things, air cooling used in the new ammonia synthesis units has reduced the water requirements ten-fold. The change-over to the double absorption contact process for the manufacture of sulphuric acid has increased the conversion of sulphur dioxide from 97.5 to 99.5% and reduced its emission to the atmosphere to less than one-sixth of its previous figure (from 0.2 to 0.03-0.05%).

Several major chemical, petrochemical and petroleum-processing plants and complexes are being designed in the Soviet Union which have provisions for ecologically optimal production schemes excluding any emissions of objectionable substances to the environment.

Chapter Thirteen

FUNDAMENTALS OF CHEMICAL MANUFACTURE DEVELOPMENT*

13.1 Statement of the Overall Problem

A chemical enterprise to-day is a chemical-engineering complex consisting of a great number of plant items and flows (or interconnections) between them. If an enterprise is to operate efficiently, many problems must be tackled well before it is built, that is, at the design stage.

The final goal in the development of a chemical-process system is to set up a highly efficient chemical manufacture, that is, a chemical processing complex, which will not only turn out the required products in the specified quantities and of the specified quality, but will do this in a most economic way. This requires that the process plant should be operated so that it will maintain a high product yield and a high product quality at a high average throughput and at low capital costs.

The design of a chemical-process system should provide for the following.

(1) It should define the *topology* of the system, that is, the arrangement and layout of the various pieces of equipment as shown in the process flowsheet. The efficiency of the system as a whole greatly depends on how correctly the required pieces of equipment are selected, the flows between them defined, and the plant items interconnected into a processing unit (or units).

(2) It should give the values of input variables which are the physical parameters of the feedstocks, and the parameters of the various physico-chemical influences exerted by the environment on operation of the system (temperature, pressure, etc.).

(3) It should specify the values of performance variables (the conversion of the feedstocks, the degree of separation of the chemical components, rate constants, mass and heat transfer coefficients, and the like).

(4) It should define the constructional variables of the system (reactor volume, vessel cross-sectional area, packed-bed depth, etc.).

(5) It should define the operating conditions to be maintained in the plant items and units of the system, such as temperature, pressure, catalyst activity, flow pattern, etc., which may affect the process rate, yield, and product quality.

* Chapter 13 has been contributed by V.N. Zaitsev.

(6) It should define the parameters of the process streams so that the system could operate under the specified conditions (mass flow rate, temperature, pressure, concentration of substances in a stream, etc.).

There are also other tasks to be handled. They include the development of automatic control for the individual processes and the complex as a whole, the choice of constructional materials, the development of methods for analysis, the maintenance of hygienic standards, etc. Special emphasis to-day is placed on the protection of the environment. Therefore, matters related to ecology must also be considered when setting up a new chemical venture. Of course, it would be impossible to launch and operate an efficient enterprise without taking into account the latest advances in chemical engineering. These include a better use of raw materials and energy, conversion of raw materials into chemicals and cogenerated power, and a change-over to plant items of an ever larger unit capacity.

When all of the above tasks are properly handled, the result will be an efficient system capable of maintaining the specified values of output variables, that is, the physical parameters of the material and energy flows at the exit from the system (mass flow rate, concentration of chemical components, temperature, pressure, viscosity, density, etc.). The reason is that the output variables taken together determine the status of a chemical-process system.

The quality of a chemical-process system can be assessed in terms of its objective function. This may be technical or economical characteristics of the chemical process. What is important is that the objective function should be chosen so that it can give an ample measure of how well a given system is operating. Therefore, it should take into account all the key features and properties of the system, the conditions in which it is operating, and how it interacts with the environment.

13.2 Systems Engineering Approach to Chemical Process Plant Development

It is seen from the complexity of the problem stated above how important it is to handle the development of a chemical process plant or complex scientifically. Among the pre-requisites for its successful solution and the integration of novel procedures in the design and analysis of industrial chemical processes are theoretical studies into the principles underlying chemical processes, wide use of computers, and the acquisition of research and design tools based on systems engineering.

It is fully realized to-day that a chemical process plant may no longer be thought of as a collection of individually designed operations and processes. Recognition of the fact that each separate unit of a plant influences all others in both obvious and subtle ways has led the designer to consider a

chemical process plant as an integral entity. Along with this has come a new concept of chemical process plant engineering and operation, combining the latest advances in chemical engineering with the capabilities of computers. This combination has come to be known as *systems engineering*.

Systems engineering poses a number of problems both in teaching and learning it.

For one thing, the literature on the subject does not give unified definitions and contains a good deal of conflicting statements.

For another, systems engineering involves a fairly complex body of mathematics. The abundance of mathematical relations, transformations and computations coupled with the use of matrix notation and graph theory, all of them not always within the grasp of an unprepared reader, puts up a serious roadblock on the way to the acquisition and use of the very idea of systems engineering.

It is not at all easy to give an overall picture of chemical-process system development. It is not a bit easier to single out the various stages in this overall task, to establish relationships between them, and to define the sequence in which they should be handled. It is these factors, and not the failure of systems engineering itself, that are responsible for the fact that very few cases have been reported in the literature where operating chemical plants have been built on the basis of systems engineering.

What follows is only a general outline of a systems engineering approach to process plant design. No mathematical procedures are included in the discussion. As a first step in getting acquainted with systems engineering, it is important to learn the principles rather than the actual mathematical procedures, so that one will know what should be used and at which stage of design work. It is hoped that such an approach to the presentation of material will to some degree make it easier for those interested to acquire a more detailed knowledge of the relevant body of mathematics examined in the literature of the subject.

13.3 Basic Concepts and Principles of Systems Engineering

The basis of the systems engineering approach is that an industrial chemical enterprise is treated as an integral system.

A *system* is an object interacting with the surroundings and having a complex internal structure, a great number of subsystems and elements interconnected by process streams and acting as an entity.

An *element* is a self-contained and presumably non-divisible unit. In chemical engineering, this is most often a vessel effecting some unit operation (this may be a chemical conversion, a diffusion operation, a heat-transport operation, etc.).

A *subsystem* is a group of elements in a processing unit possessing a certain degree of integrity and pursuing an objective of its own. This is a self-contained division of a system.

Both a system's elements and subsystems are interconnected by various material, energy, heat, and information flows. These flows reflect the transport of material, heat, or energy between the elements by physical streams, while any changes in a stream take place in the elements themselves.

An assemblage of elements and interconnecting flows makes up the system's structure.

The basic principles of systems engineering may be summed up as follows.

- (1) Presentation of an object as a system.
- (2) Investigation of the object in so far as it is presented as a system.

This implies that systems engineering's strategy should proceed from the whole to a part, from the system-forming relations and properties, that is the structure, to the elements (and not the other way around as happens with an empirical approach). In an analysis of a chemical-process system one is concerned with an element's pivotal properties, that is, those which determine its interaction with the other system elements or affect the properties of the system as a whole, rather than with the internal properties and structure of the element.

The elements of a chemical-process system can be interconnected and interrelated in a variety of ways. The strength of these interconnections and interrelations (constraints and flows) depends on how critical they are. It is the objective of a systems-engineering analysis to determine which are critical and which are not.

The above approach constitutes only a prelude to a systems-engineering analysis, and the analysis proper begins when one sets out to determine the general properties, called the system parameters, that characterize the system in question, the type to which it belongs, and the overall relations that operate within a given type of systems.

Reliance on the overall relations and the association of the systems engineering approach to the general theory of systems is a major distinction of, and an advantage offered by, systems engineering. With this approach, one may establish and exploit deep structural and functional analogies between systems belonging to different levels of matter, investigated in different fields of science.

13.4 The Chemical Enterprise as a Complex System

Any chemical manufacture involves a sequence of three basic stages: preparation of feedstocks, the chemical conversion proper, and separation

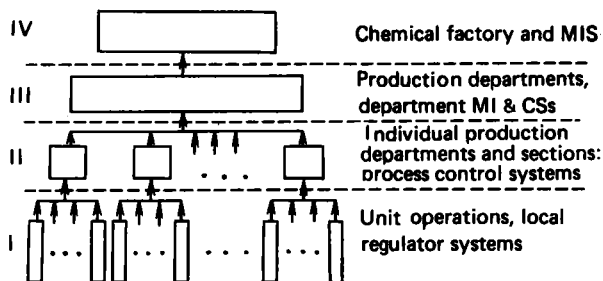


Fig. 13.1 Hierarchical structure of a chemical complex

of end products. The three stages are implemented within a single complex chemical-process system.

Chemical-process systems that may be identified with complete plants have the following distinct features:

- (1) There is a common goal of operation — to turn out a product.
- (2) The system is large — it has a great number of component elements interconnected by a great number of flows.
- (3) The operation of a system is characterized by a great number of variables.
- (4) The system behaves in a complex manner — a change in the operating conditions of one plant item may affect the performance of the entire plant.
- (5) Plant and process control is automated to a very high degree.
- (6) There is a need for supervisory and control information flows between the various elements of a chemical-process system and their respective controllers.

In view of the above attributes, a chemical enterprise may be treated as a complex system.

The presentation of a chemical enterprise as a system presupposes its decomposability into interrelated subsystems. The subsystems are in subordination which may be depicted as a hierarchical structure consisting of three or four hierarchical levels or ranks.

The first, or lowest, rank of this hierarchical structure includes *unit operations* and *unit processes of chemical engineering* (operations based on heat transfer, fluid mechanics, mass transfer, and mechanical principles, and also chemical conversions) along with their respective local automatic control systems, mainly of the *regulator type*. The unit operations and unit processes are effected in plant items where the process streams passing through them are subjected to physical and chemical influences.

The second rank of the hierarchy includes *processing units* which are interrelated assemblages of plant items, unit operations and unit processes,

each dedicated to a particular task. Most often, these processing units are departments (shops) or their sections (bays). The second level of the hierarchy uses *automatic process control systems*, mainly of the servo type, to coordinate the operation of the various plant items and to distribute the process streams among them in an optimal manner.

The third level of the hierarchy includes *chemical plants* or *manufactures* each of which may consist of several processing units and which turn out end products. It uses both *automatic process control* and *management information systems*, MI&CS, responsible for the functioning of the plants.

The fourth level is the *enterprise*, or *complex*, as a whole. It uses a management information system, MIS, adapted to the needs of the complex as an entity.

A distinction of the hierarchical structure of a chemical complex is not only that it presents subordination between its levels, but also that it defines the form of interrelation between the subsystems at the same level.

13.5 The Overall Strategy of Systems Engineering. Basic Steps in the Development of a Chemical-Process System

In practice, a process and plant designer may face any one or both of two basic tasks: one is to design and engineer new high-performance processes and plant, and the other is to upgrade those already in service. Each task is usually achieved in several stages, carried out in parallel or consecutively. For a proper evaluation of the volume of work involved, the various steps in its execution, the interrelation between them, and the sequence in which they should be performed, it is convenient to visualize the development and/or operation of a chemical-process system as a multi-level task, each level differing from another in complexity.

The first level in this overall task is to build mathematical models for the individual elements and, on their basis, a complete mathematical model for the system as a whole.

The mathematical model should reflect the essence of the system's functioning as an entity. For this purpose, the model should include quantitative relations that describe the most important aspects of the chemical manufacture. Above all, the mathematical model should reflect the operations that take place in the system elements, the flows between the elements, and the dynamics of the interaction between the elements and subsystems of a complex system. Also, it is necessary, already at the model building stage, to choose the objective function — a performance criterion — for the system, and to establish its functional dependence on the various factors so that its numerical values could be found for the system operating under different conditions.

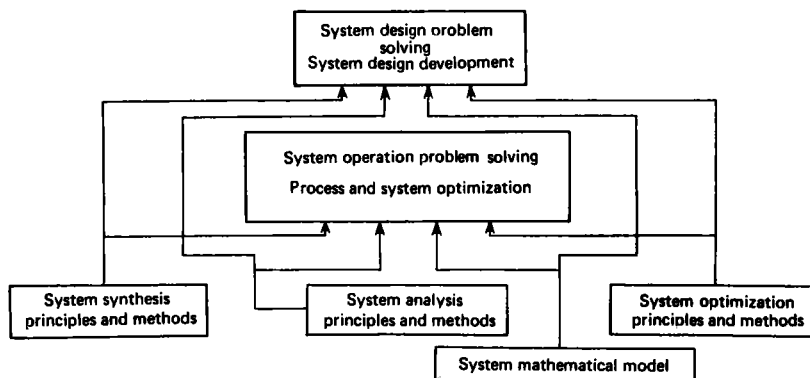


Fig. 13.2 Key steps in the development of a chemical-process system

Mathematically, the model-building step reduces to finding the manner in which the output variables of the system depend on the variables that may affect the system's operation. These latter variables are:

(1) Input variables (quantity of raw material, its composition, etc.). Let these factors be designated as $X_1, X_2, \dots, X_n$, and the complete set of these factors will be given the symbol $\bar{X}$ and called the input variable vector.

(2) External variables, such as temperature, pressure, etc. They are assigned the symbol $\bar{V}$ and will be referred to as the external variable vector.

(3) Performance variables of the system's elements. Their vector is $\bar{D}$.

(4) Constructional variables. Their vector is $\bar{K}$.

All of the above factors are taken into account when building a mathematical model for an individual element. Then the mathematical model of an individual element, showing how the output variables (quantity of product, product composition, etc.) depend on the system-affecting variables, will take the form:

$$\bar{Y} = f(\bar{X}, \bar{V}, \bar{D}, \bar{K}) \quad (13.1)$$

where $\bar{Y}$ is the output variable vector.

If a system has N elements (plant items), then models similar to the above one can be built for all of them:

$$\bar{Y}_i = F_i(\bar{X}_i, \bar{V}_i, \bar{D}_i, \bar{K}_i) \quad (13.2)$$

where i is the number of any element from 1 to N .

Of course, for each element this functional relation will take a form different from that applying to another element. In Eq. (13.2) this fact is shown by using the symbol F_i instead of the f used in Eq. (13.1). It

designates a vector function of a vector of variables, that is, a set of the various functions applicable to a given set of plant items.

After mathematical models have been built for all the system elements, the next step is to build a mathematical model for the entire chemical-process system.

As already noted, it would be wrong to pass judgement on the performance of an entire system (an entire plant or complex) from that of the component elements (the plant items) analysed separately. The optimal behaviour of a system is not an additive function of its elements even though they may be optimally built. Therefore, the mathematical model of a chemical-process system cannot be a simple collection of the mathematic models built for its elements. When building it, two more factors should be considered in addition to the four factors noted above, namely:

(1) In a system, its elements (plant items) may be interconnected in any one of several ways (in any one of several sequences and by flows differing in nature). In other words, a system may have any one of several process topologies. (We will use the symbol G to designate different topologies.) The process topology has a direct bearing on the performance of the entire system and must therefore be reflected in a mathematical model.

(2) The internal connections (flows) that arise when the elements are put together into a system have each a set of parameters of its own. They, too, may affect the performance of the plant as a whole, and so they should be included in the system's mathematical model. (We will use the symbol $\bar{L}$ to designate the internal flow variable vector.)

Then the model of a chemical-process system takes the form

$$\bar{Y}_i = F_i(\bar{X}_i, \bar{V}_i, \bar{D}_i, \bar{K}_i, \bar{L}_i, G) \quad (13.3)$$

Apart from the system's output variables $\bar{Y}_i$, the development of a chemical-process system involves evaluating the system's objective function E for each of its alternative designs. Therefore, the mathematical model of a chemical-process system should, in addition to relations of the form of Eq. (13.3), also include a functional relation with which to evaluate E :

$$E = \Psi(\bar{Y}_i, \bar{V}, \bar{D}, \bar{K}, \bar{L}, G) \quad (13.4)$$

If this mathematical model is to be of practical use in the subsequent work, it is necessary to develop an algorithm so that it can be set up and run on a computer, and to check it for 'closeness of fit' to the plant in question.

The first stage in the development of a chemical-process system terminates in building mathematical models for the system's elements and subsystems. After they have been built, the designer may proceed to the second stage.

An analysis of a chemical-process system has as its objective to study the properties and performance of the entire system from its mathematical model. The system's properties depend on the state variables and characteristics of its elements and the structure of the flows between them. In the course of an analysis, it is necessary to assess the effect of these factors on the system's output variables which characterize the system's state.

At the first stage in the system development which yields mathematical models for its elements and subsystems, it is too early to speak of a model for the entire system because it depends on the system's structure which has not yet been defined. A complete mathematical model for an entire system is built at the system's analysis stage, proceeding from a particular topology. As a result of the analysis, the state characteristics (output variables) of the entire system are quantitatively related to the variables and characteristics of the individual elements.

By re-arranging the process topology (the structure of the flows that interconnect the elements and subsystems) and using different values for the process and constructional variables of the elements, the designer builds and solves several models of the system. From their comparison, he may form an idea about their merits and demerits.

In the light of the foregoing, we may alternatively formulate the goal of a system's analysis as follows: *Build a complete mathematical model for the chemical-process system in question from the mathematical models of its individual elements and process topology with a view to determining the variables of the output flows under the specified process conditions and variables of the input flows.*

Of course, a complete model can be built and solved only after the chemical-process system has been synthesized. That is, a system's analysis cannot be separated from its synthesis.

The synthesis stage has as its objective to develop a high-performance chemical-process system. In achieving this goal, it is necessary above all to choose an optimal process topology, G (that is, to choose the number and type of plant items and to establish the character of interconnecting flows), then to evaluate the system's input variables $\bar{X}$, the element's process variables $\bar{D}$, and the internal flow variables $\bar{L}$.

The above set of variables should be combined in such a way that the system will operate efficiently, that is, its objective function E is maximized. In other words, the goal of a system's synthesis is to find such values for the variables

$$G = G(\bar{Y}, \bar{V}, \bar{K}, E_n^*) \quad (13.5)$$

$$\bar{X} = f_1(\bar{Y}, \bar{V}, \bar{K}, E_n^*) \quad (13.6)$$

$$\bar{D} = f_2(\bar{Y}, \bar{V}, \bar{K}, E_n^*) \quad (13.7)$$

$$\bar{L} = f_3(\bar{Y}, \bar{V}, \bar{K}, E_n^*) \quad (13.8)$$

that the system's objective function E has an optimal value:

$$E^* = \text{opt } \varphi(\bar{Y}, \bar{V}, \bar{D}, \bar{K}, \bar{L}, G) \quad (13.9)$$

where E^* is an optimal value of the objective function E , and E_n^* is its maximum value.

It is seen from the foregoing that the synthesis of a chemical-process system is closely related to the system's optimization, that is, a procedure whereby an optimal value, E^* , of the system's objective function is established. From a mathematical point of view, system synthesis reduces to system optimization. The objective functions most often chosen for chemical-process systems are those of economic nature (return on investment, profit, discounted costs, manufacturing cost, etc.) or, sometimes they may be technical criteria, such as the overall yield of the product.

The functional dependence of the objective function E on the factors that affect it is established at the model-building stage, Eq. (13.4), and the applicable solution algorithm is developed at the analysis stage.

From the definition of a chemical-process system's analysis, synthesis and optimization it is seen that the three stages are intimately related to each other. A feature common to them is that they are all carried out on the basis of the system's mathematical model. On the other hand, each stage has a basic goal of its own. At the model-building stage it is the derivation of relations between the system variables, as evidenced by Eqs. (13.2); at the analysis stage it is a study, on the basis of these equations, into the system's properties (for which purpose the system's complete mathematical model is built and solved); and at the synthesis stage it is the development and optimization of the system's alternative designs from among which the final version is chosen.

For better insight into how the synthesis, analysis, and optimization stages are interrelated, we will show, albeit in a general outline, the sequence in which they are applied in practice. To begin with, an initial version of the system is synthesized. Following that, this version is subjected to a complete analysis on the basis of its model. During this analysis, the designer evaluates, in addition to the system's output variables, also its objective function. The synthesis and analysis of the initial version constitute the first phase in the development of a chemical-process system.

The findings of the analysis form the basis for decision-making during the second phase when the system is again synthesized but at a higher level of performance. The improved version of the system is again analysed, and the designer decides on the course of action during the third phase concerned with the development of a still better version of the system, and so on. At each phase and for each version, the designer compares the respective objective functions. This cyclic procedure of synthesis and analysis is repeated until an optimal value is obtained for the system's objective func-

tion, that is, the system's synthesis and analysis is accompanied by its optimization.

This combination of a system's synthesis, analysis and optimization on the basis of its mathematical model tackles the most challenging problems related to levels III and IV of the overall task — the intensification and optimization of existing processes and plants and the development of new chemical complexes by an optimum design procedure.

At present there is a growing trend to replace the conventional process and plant design procedures by an optimum design procedure. The fundamental difference between these two approaches consists in that with the conventional design procedure the choice of what seems to be an optimum version is not sufficiently justified from the view-point of the desired results. This form of design often reduces to a scale-up of laboratory-developed plant items and reaction schemes which are not always optimum for industrial practice. As a rule, the laboratory only determines the constructional and technical variables of the reaction vessels and plant items, but neglects the interrelation and interaction between them. The process topology is chosen without an analysis of the likely alternatives. This approach is bound to fail in developing a high-performance chemical manufacture.

With optimum design, the final version is chosen by following a specially devised strategy which uses the mathematically proven trial-and-error procedure with each trial involving a great number of plant item types, flowsheets and sets of operating conditions. Sometimes, their overall number may run into many hundreds. This task can successfully be handled by computer-aided design (CAD) systems.

A typical CAD system consists of a number of devices. One stores data about the process (such as the mathematical models of the chemical-process system's elements, physico-chemical constants, the properties of the participants in the process, etc.). Others are responsible for actions which support the operation of the CAD system, such as input of design data, the main executive subroutine, and output of the results.

In computer-aided design, the mathematical model of a chemical-engineering system's individual element is presented as a set of mathematical models representing the unit operators involved. The model of a unit operator is referred to as a module. It usually takes several modules to describe one element of a chemical-process system. As a rule, these are standard modules which may be used to model any element of the system. Using the standard programs of the mathematical models representing the unit operators, the mathematical models of the system's elements can be built on the modularity principle.

13.6 Models of Chemical-Process Systems

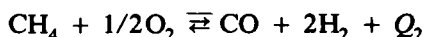
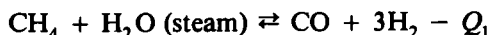
All models of chemical-process systems may be classed into *qualitative* (generalized) and *mathematical*, and these may further be subdivided into various kinds.

Qualitative (generalized) models may be operation descriptive and iconographic.

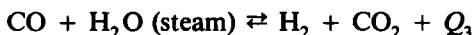
Operation descriptive models are verbal descriptions of how the respective systems are functioning. Such a description states the basic chemical reactions by which the end product is obtained (the chemical reaction scheme of a process) and outlines the operations that take place in the various plant items, lists the feedstock composition, process variables, and the like. In practice, an operation descriptive model may take the form of design and development documentation and specifications.

Iconographic models refer to graphics or drawings. A generalized iconographic model gives only a qualitative idea about how a given system is functioning. These models come in several forms of diagrams, such as generalized block diagrams, detailed block diagrams, operation (or operator) diagrams, and process flowsheets*.

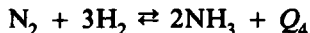
To show how the various diagrams are drawn up, we will use ammonia synthesis as an example. The first step is to set up the *chemical reaction scheme*, that is, to write the reactions by which the desired product is obtained. To begin with, methane is converted to yield hydrogen:



The carbon monoxide thus obtained is then converted with steam to give hydrogen:



Since the conversion step involves the use of an air-steam mixture rather than pure steam, the reaction products carry some nitrogen in addition to hydrogen — thus a hydrogen-nitrogen ($\text{H}_2 + \text{N}_2$) mixture is obtained. The next step is the ammonia synthesis proper:



A simplified process flowsheet of an ammonia synthesis unit is shown in Fig. 13.4. It is simplified in the sense that some secondary pieces of equipment are omitted.

* Other authors class them all as “flowsheets” and add a descriptor to tell one subdivision from another. For example, “process flowsheet”, “engineering flowsheet”, etc. See J. R. Backhurst, J. H. Harker, “Process Plant Design”, Elsevier, 1973 — *Translator's note*.

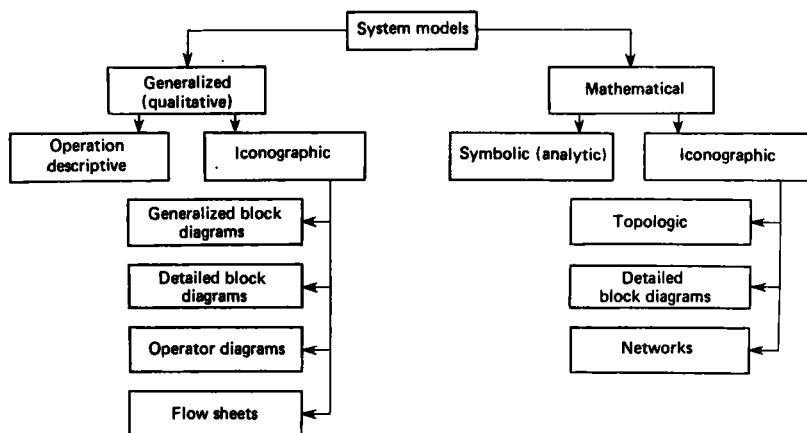


Fig. 13.3 Models of chemical-process systems

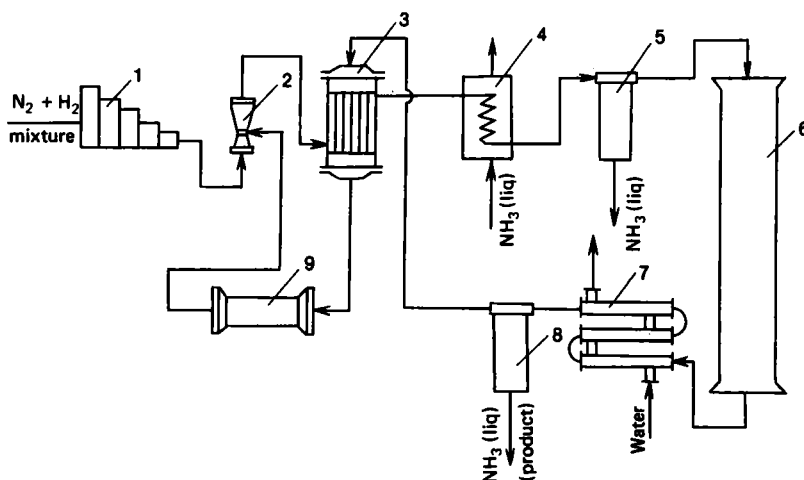


Fig. 13.4 Simplified process flowsheet of an ammonia synthesis unit:

1, compressor; 2, injector; 3, heat exchanger; 4, liquid-ammonia vaporizer; 5, separator; 6, ammonia synthesis reactor; 7, water cooler; 8, separator; 9, circulating compressor

Referring to the flowsheet, the $H_2 + N_2$ mixture enters a compressor, 1, which compresses it to a pressure of 30 MPa. In an injector, 2, the compressed mixture is mixed with the unreacted $H_2 + N_2$ returned from the converter, and is cooled first in a heat-exchanger, 3, then in a liquid-ammonia vaporizer, 4. The cooling operation causes the NH_3 always present in the $H_2 + N_2$ mixture to condense. The liquid ammonia is separated in a separator, 5, and the $H_2 + N_2$ mixture goes to the ammonia synthesis

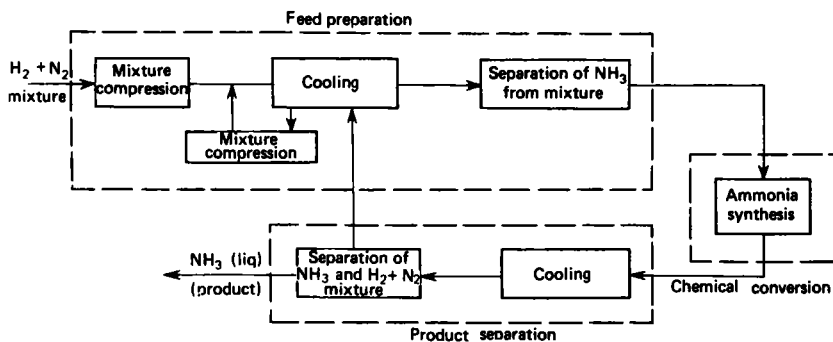


Fig. 13.5 Generalized block diagram of ammonia production

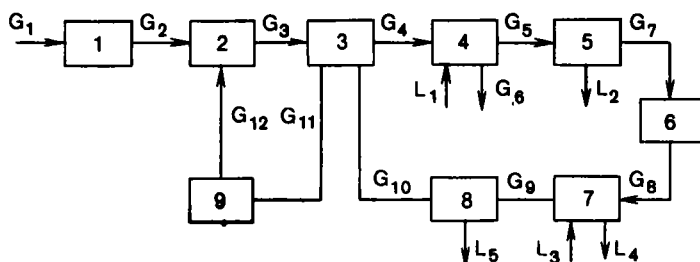


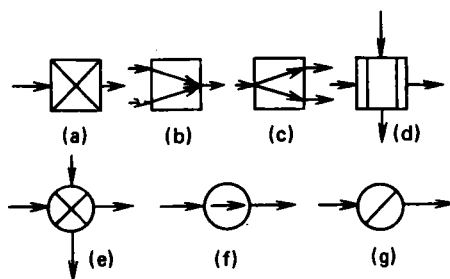
Fig. 13.6 Detailed block diagram of ammonia synthesis:

1, compressor; 2, injector; 3, heat exchanger; 4, liquid-ammonia vaporizer; 5, separator; 6, ammonia synthesis reactor; 7, water cooler; 8, separator; 9, circulating compressor; G_1 through G_{12} , gas streams; L_1 through L_5 , liquid streams

Fig. 13.7 Process operators:

Primary: a, chemical conversion; b, mixing; c, separation; d, inter-phase mass transfer

Secondary: e, heating or cooling; f, compression or expansion; g, change in state of matter



reactor, 6, where the synthesis reaction takes place. The product ammonia is separated from the unreacted $H_2 + N_2$ mixture, first by cooling in a water cooler, 7, then in a separator, 8. The remaining mixture at a pressure of 28 MPa is compressed to 30 MPa by a recycle compressor, 9, and is recycled to the process for the further chemical conversion.

A *generalized block diagram* gives an overall idea about the operation of a chemical-process system. It shows as separate blocks the key plant units (subsystems) that perform specific operations and also the process flows that interconnect the units. A generalized block diagram thus shows what operations are involved in a given process and in which sequence. It tells nothing about the individual elements. A generalized block diagram for ammonia synthesis is shown in Fig. 13.5.

A *detailed block diagram* of a chemical-process system displays all the system's elements as blocks each having several inlets (inputs) and exits (outputs), and also the flows that interconnect them. As is with a generalized block diagram, the detailed block diagram tells us nothing about the types of plant items, but the flows between the blocks indicate the directions in which the system's material and energy streams move (Fig. 13.6).

An *operator diagram*, in contrast to the two previous forms, graphically displays the physico-chemical principles underlying the operations and conversions taking place in the system. For this purpose, each element of a chemical-process system is represented by the respective unit operator which causes the inlet material and/or energy streams to undergo qualitative or quantitative changes, that is, effects the operation described by Eq. 13.1.

The unit operators may be classed into primary and secondary. The primary operators (Fig. 13.7) provide for progress of the system towards the specified objective. Among them are the operators involving chemical conversion, interphase mass transfer, mixing, and separation.

The secondary operators have as their objective to enhance the system's performance by bringing about appropriate changes in its energy and phase state. These are heating and cooling operators, compression and expansion operators, and operators responsible for changes in the state of matter (condensation, evaporation, dissolution).

The individual operators interact through the agency of interconnecting flows. Each flow represents a particular material or energy stream referred to as a *process stream*.

An operator diagram for ammonia synthesis is shown in Fig. 13.8.

A *process flowsheet* gives the fullest qualitative idea about the process involved. Each process element is displayed by a standard flowsheet symbol, and the flows are indicated by arrowheads. By reference to a process flowsheet, one can readily form an idea about the types of plant items, the manner in which they are arranged and interconnected, and the sequence in which the individual operations are effected. Sometimes a process flowsheet may be supplemented with short notes on the chemical composition and other important attributes of the feed, intermediates, and products. Sometimes, the plant items will be drawn to scale so as to give an idea about their relative size and construction.

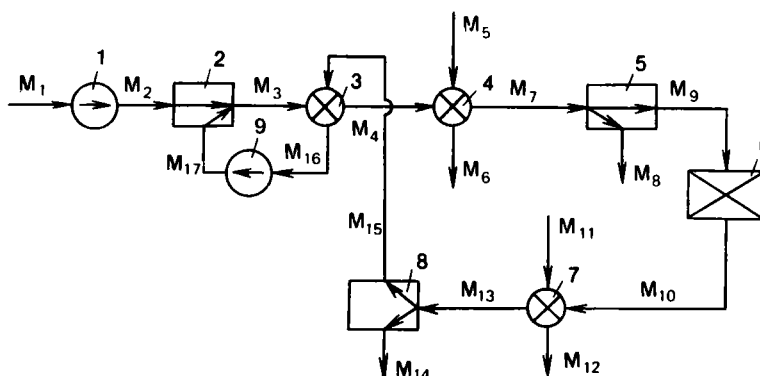


Fig. 13.8 Operator flowsheet for ammonia synthesis:

1, compressor; 2, injector; 3, heat exchanger; 4, ammonia cooler (liquid-ammonia vaporizer); 5, separator; 6, ammonia synthesis reactor; 7, water cooler; 8, separator; 9, circulating compressor; M_1 through M_{17} , streams

Process flowsheets may be used to depict a chemical-process system both at the design stage and during operation. For its designer, it is a prototype offering a first glimpse at the contemplated system.

A process flowsheet for the entire ammonia plant is shown in Fig. 14.15, and that for its NH_3 synthesis unit in Fig. 13.4.

So far we have been dealing with one class of models representing chemical-process systems — qualitative (generalized) models. The other class — mathematical models — offers a quantitative description of the process. They, too, may be of one of several forms. Thus, all mathematical models may be classed into symbolic and iconographic (Fig. 13.3).

A *symbolic (analytical) model* is a set of mathematical formulas, equations, and inequalities. They tell us about the physical state of the process streams at the exit from the system as a function of the factors effecting the system, that is, the input variables $\bar{X}$, external variables $\bar{V}$, technical or performance variables $\bar{D}$, and constructional variables $\bar{K}$ of the system's elements. For an individual element of the system, these relations take the form of the already familiar equation (13.1).

Since a chemical-process system is an assemblage of interrelated elements, the system's symbolic model includes above all the symbolic models of all its elements. However, it should also include the flows that exist between the elements. Thus, the fact that a flow leaves the k th unit and enters the n th unit (where k and n are the numbers of the elements interconnected by the same flow) will be shown by a relation of the form

$$\bar{Y}_k = \bar{X}_n \quad (13.10)$$

In practice, some constraints will always be imposed on some variables.

Therefore, the mathematical model will also include relations of the form

$$H_i(\bar{X}_i, \bar{Y}_i, \bar{D}_i, \bar{K}_i) \geq 0 \quad (13.11)$$

where H_i is the vector function of process constraints on the state variables of the flows and elements of the chemical-process system.

Iconographic mathematical models give a graphical representation of either the qualitative properties of the system's structure from which one can derive the system's quantitative characteristics, or the functional mathematical relations between the independent and dependent variables entering into the system's symbolic model, or the logic of the functional relations between the equations and information variables entering into the system's symbolic model.

Whereas generalized iconographic models give only qualitative information about the process, mathematical iconographic models are related to the quantitative characteristics of the system. Therefore, they are indispensable in the analysis, synthesis, and optimization of complex chemical-process systems.

Mathematical iconographic models may be classed into three groups: topological models, generalized block-diagrams, and network models.

Topological models take the form of graphs. A graph, as defined in general graph theory, is a set of points, termed vertices or nodes, interconnected by a set of non-intersecting straight-line segments, broken lines, or curves, termed edges for undirected (unoriented) graphs or arcs for directed (oriented) graphs.

In chemical processes, the vertices of a graph are often its plant items, and the arcs represent the directed flows between them.

There are several forms of topological models, or graphs, that are applicable to chemical-process systems. Their choice depends on which properties of the elements and which flows between them are of interest to the designer or the analyst.

Suppose that we are to draw topological models for the ammonia synthesis process whose operator diagram appears in Fig. 13.8. Operator 1 compresses the feedstock (an $H_2 + N_2$ mixture), operator 2 mixes it with the recycled unreacted feedstock that has already been to the converter, operators 3 and 4 cool the $H_2 + N_2$ mixture, operator 5 separates the condensed ammonia from the mixture, operator 6 effects the chemical conversion, operator 7 effects water cooling, operator 8 separates the product ammonia from the unreacted feed, and operator 9 compresses the $H_2 + N_2$ mixture.

Each i th physical stream, or simply stream of the system (in our case there are a total of 17 such streams) is characterized by a set of variables as follows:

— the overall mass flow rate g_i of the stream;

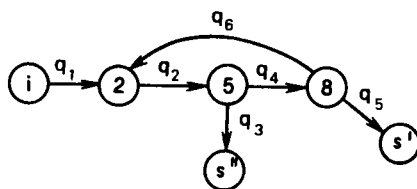


Fig. 13.9 Overall material flow graph of a chemical-process system:

2, 5, 8 — vertices representing the correspondingly numbered operators in the operator flowsheet of Fig. 13.8; i , source representing admission of feedstock with stream M_1 ; s' and s'' , drains of products with streams M_7 and M_{13} ; q_1 through q_6 , overall mass flows

- the mass flow rate g_{ij} of component j (we have a total of three components — NH_3 , H_2 , and N_2) in the i th stream;
- the concentration C_{ij} of the j th component in the i th stream;
- the temperature T_i of the i th stream, and
- the enthalpy H_i of the i th stream.

In developing topological models for the scheme presented in Fig. 13.8, we may be interested in its various aspects. Suppose that we need to know the overall material flows between the elements of the system shown in the diagram. An applicable graph appears in Fig. 13.9.

Since we are interested in changes that take place in the overall mass flow rate of the system's components, we should develop the graph using only those elements from the operator diagram where the mass flow rate undergoes a change. They will constitute the vertices of our graph.

Operators 1, 3, 4, 6, 7, and 9 (see Fig. 13.8) do not change the overall mass flow rates. (Operators 1 and 9 change the pressure, operators 3, 4, 6, and 7 change the temperature, and operator 6 effects the chemical conversion, changes the composition and temperature of the stream but the overall mass flow rate remains unchanged.) Therefore, the graph will not contain vertices representing these operators. On the other hand, the graph should reflect the admission of the feed to and withdrawal of the product from the system. Therefore the graph is expanded to include one more vertex or node, designated as i for the feedstock source, and two more vertices or nodes, designated as s' and s'' for the product sinks. Source i corresponds to the total quantity of feed admitted to the system with flow M_1 . Sink s' corresponds to the quantity of product withdrawn from the system with flow M_{14} , and sink s'' to the quantity of product (NH_3) withdrawn with M_8 .

Since the graph shown in Fig. 13.9 is drawn up in terms of overall mass flow rate, it is quite aptly called the overall material flow graph of the system. Its vertices represent the system's elements that change the overall mass flow rates of the streams, and its arcs are the material flows representing the overall mass flow rate of the system's streams.

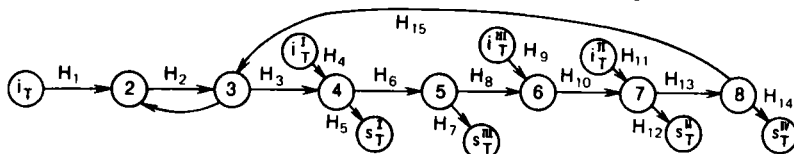


Fig. 13.10 Heat flow graph of a chemical-process system:

2 through 8, vertices representing the correspondingly numbered operators in the operator flowsheet of Fig. 13.8; i_T , i_T' and i_T'' , sources of heat entering the system with streams M_1 , M_6 and M_{12} ; i_T''' , source of heat evolved by an exothermic reaction; s_T , s_T^I , s_T^{II} and s_T^{IV} , sinks of heat with streams M_1 , M_{13} , M_9 and M_{14} ; H_1 through H_{16} , heat flows

Other forms of graphs may be drawn up for the system shown in Fig. 13.8. For example, there may be a graph drawn in terms of the mass flow rate of any individual component in the system's streams rather than in terms of the overall mass flow rate. Accordingly, such a graph will be called a component material flow graph.

If the process in question interests us from a thermal point of view, we can draw up a heat flow graph. Its vertices represent the system's elements that change the quantity of heat in the streams, and also the heat sources and sinks of the system. The arcs represent the heat flows. A heat flow graph for the system in question appears in Fig. 13.10. In addition to the system's operators that change the heat flows, the graph contains vertices representing the system's heat sources and sinks.

The material and heat flow graphs we have just described reflect the topology of the process as such. We may, however, set up graphs reflecting the topology of the equations that make up the system's symbolic model. These are *signal flow graphs* — they display functional relations between the information variables that enter into the equations making up the symbolic model. These variables are referred to signals, and this explains why these graphs are referred to as signal flow graphs. Apart from representing the equations of the system's symbolic model, a signal flow graph reflects the cause-and-effect relations that exist between the system variables.

In a signal flow graph, the vertices represent signals, that is, the system's variables of state and properties. The source vertices represent independent variables, and the sink vertices represent dependent variables with respect to which the set of equations can be solved in explicit form. The arcs in a signal flow graph have an associated quantity called the *gain* or the *transfer function* which describes the relation between the signals.

Still other forms of graphs could be developed, but we close their examination with what we have done. A few words are in order about other sub-groups of iconographic models. They are generalized block diagrams and network models.

A *generalized block diagram* is an iconographic mathematical model which corresponds to a symbolic mathematical model. In it, every process

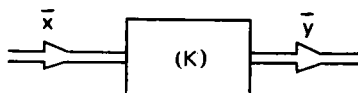


Fig. 13.11 Block of a detailed block diagram:

$\bar{X}$, input variable vector; $\bar{Y}$, output variable vector; (K) , set of gains in matrix notation

operator is shown as a block, as in Fig. 13.11. Each block is a mathematical model (a set of gains and transfer functions) of the respective process operator and relates the block's input variable vector to its output variable vector. Then the generalized block diagram of an entire chemical-process system will be a collection of such individual blocks interconnected by the state variable vectors of the respective flows in the system.

Generalized block diagrams and signal flow graphs reflect various aspects of a symbolic mathematical model. They are in a one-to-one correspondence: a directed (oriented) branch in a block diagram maps into a vertex in the respective signal flow graph. (In each case, this is a set of state variables applicable to the system's process flow.) By the same token, each block maps into a directed (oriented) branch in the signal flow graph. (In each case this is a set of gains or transfer functions.)

Network models are iconographic models drawn up to show the progress of design, operation, and management as applied to chemical-process systems.

13.7 Tasks of Chemical-Process System Analysis, Synthesis and Optimization

The tasks facing the designer at the second level of a chemical plant's development, that is, its analysis, synthesis and optimization, are closely interrelated and have to be handled together in practice.

In the analysis and synthesis of a chemical-process system, the designer runs into a number of difficulties of both methodological and computational nature. This stems from the fact that any chemical-process system is multivariable in terms of both its elements described by a great number of differential and finite-difference equations, and their functions. The matter is complicated still more because the elements are interrelated and affect one another.

When analysing the operation of a chemical-process system, the need exists to develop a complete mathematical model for the system from known mathematical models of its elements and from the specified process topology. Even for state-of-the-art computers, a single run of a system's complete model would entail a multitude of difficulties and take up a lot of time. In fact, the situation is far more complicated if we recall that in system synthesis we have to analyse and optimize the system more than

once, that is, to obtain a complete solution of the model by a trial-and-error procedure for a great number of alternative process topologies. Unless a scientific approach is taken, the great number of system elements and of flows between them would lead to a huge multitude of alternatives hardly manageable even by advanced computers.

Therefore, the high-priority tasks in developing a chemical-process system are to generate optimal algorithms for a computer to solve the multidimensional sets of equations which make up the mathematical models, and to develop an optimal computational procedure establishing the sequence in which the output variables of the entire system could be derived from the mathematical models of the system's elements. The choice of an optimal strategy is no less important at the synthesis and optimization stages in the development of a chemical-process system.

Work on optimal strategies for all stages in the development of a complex chemical-process system is substantially eased through the use of topological models. Matrix notation, too, is a great help when one has to do with symbolic and topological models. The presentation of an element's symbolic model in matrix notation at the analysis stage is convenient because a wealth of important information about the contemplated system can be given in a compact and instructive way. Also, matrix notation is convenient for use on computers.

If in a symbolic model which may generally be written as Eq. (13.1) the relations between the input and output variables are described by linear functions, the model of each i th element may be written in matrix notation as

$$(Y_{m1}^i) = (R_{mn}^i) \times (X_{n1}^i) \quad (13.12)$$

where: m = number of output variables

n = number of input variables

(X_{n1}^i) = input variable vector

(Y_{m1}^i) = output variable vector

(R_{mn}^i) = transformation or operational matrix

The elements of the transformation matrix reflect the relation between the input and output variables. Each of its columns represents an input variable, and each row represents an output variable. Each element of the matrix is the transfer function that establishes the form of functional relation between the respective input and output variables. The form of this relation is identified or, which is the same, the matrix elements are determined on the basis of experimental data collected by tests while developing the respective mathematical model. The coefficients of the transformation matrix are found by solving the equations of the mathematical model analytically.

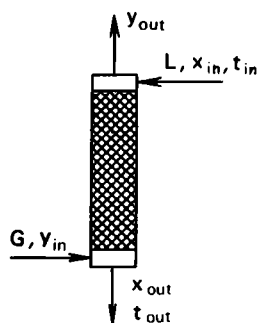


Fig. 13.12 Packed absorption column

How this looks like may be demonstrated by invoking the following example. Suppose that we are concerned with the absorption of reactant A present as the gas phase by an active component B present as the liquid phase (Fig. 13.12). The course of the process is governed by the following input variables:

G , the mass flow rate of the gas phase

L , the mass flow rate of the liquid phase

t_{in} , the temperature of the inlet liquid stream

$x_{B,in}$, the concentration of component B in the inlet liquid stream

$y_{A,in}$, the concentration of component A in the inlet gas stream

Taken together, the above quantities constitute the input variable vector.

The output variable vector of the absorber will include the following quantities:

$y_{A,out}$, the concentration of component A in the outlet gas stream

$x_{B,out}$, the concentration of component B in the outlet liquid stream

t_{out} , the temperature of the outlet stream

Suppose further that the above process has been studied experimentally and that its symbolic mathematical model (the coefficients of the equations) have been found. For convenience and ease of grasp, this model may be written in matrix form. Then it will look like this:

$$\begin{pmatrix} y_{A,out} \\ x_{B,out} \\ t_{out} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} \end{pmatrix} \times \begin{pmatrix} G \\ L \\ y_{A,in} \\ x_{B,in} \\ t_{in} \\ 1 \end{pmatrix} \quad (13.13)$$

The output variables are collected into a column vector on the left and the input variables into a column vector on the right (with a 1 added to account for the free terms in the model equations), with the transformation matrix placed in between (some of its elements may be zeros).

The matrix representation of a model enables the designer to determine the output variables directly if he knows the input variables. For example the concentration of component *A* in the exit gas stream, $y_{A,out}$, may be found by the equation derived from the transformation matrix:

$$y_{A,out} = a_{11} G + a_{12} L + a_{13} y_{A,in} + a_{14} x_{B,in} + a_{15} t_{in} + a_{16} \quad (13.14)$$

In an analysis of a chemical-process system it is very useful that, similarly to a symbolic model, the information contained in a graph may be presented in algebraic form, that is, as matrices. This connection between a graph and a matrix eases practical use of topological procedures in the mathematical description of a chemical-process system. Using various matrices, the designer is in a position to translate the structural features of a system into a language of the numbers appearing in mathematical equations. Among other things, by reference to the matrices set up for a graph he may establish whether or not any vertex of the graph is connected to any other of its vertices, glean quite a lot about the system's structure and be able not only to describe the process quantitatively but also to develop an optimal strategy for the system's analysis.

An optimal strategy is important not only during the analysis stage when setting up and solving a system's complete model. It is as essential when tackling the tasks of the system's synthesis and optimization. It should provide for not only the sequence in which the various steps (procedures) should be effected when synthesizing a system of a particular topology, but also the technique and sequence to be adhered to when testing the alternative topologies by trial and error.

The algorithms that are developed to reflect the above sequences and procedures substantially cut down the volume of work involved in a system's development, and lead faster to the system's alternative design that results in an optimal value for its objective function.

In developing a mathematical approach to chemical process design, any one of several principles practised in the synthesis of chemical-process systems may be used.

The decomposition principle. Here a mathematical formalism is applied to the functional decomposition method which has so far been employed intuitively. Since the systems he has to do with are extremely complex, the designer is forced to consecutively decompose the overall task into a number of simpler subtasks. At first, the entire chemical manufacture is divided into functional subsystems, then each subsystem is subdivided into plant item levels (element levels).

Instead of the overall task of the system's synthesis, the designer solves the several subtasks, and for each he looks for a technological solution which is abreast of the state-of-the-art advances in process plant. From among several alternative process topologies and process plant designs, he chooses such that will assure an optimal value for the objective function of the system being synthesized.

The heuristic principle. Here a mathematical formalism is applied to the intuitive heuristic method widely practised by designers. With it, the designer intuitively chooses what he feels is the best design for his process and plant without testing all alternatives by trial and error.

Although such a choice is based on intuition rather than on proof, this does not impair its value because it uses the intuitive factors and rules which rest on the wealth of knowledge and past experience gained by a team of highly competent designers.

The integrated hypothesis principle. Here, one consecutively develops, analyzes and optimizes a generalized hypothetical structure for the contemplated chemical-process system. This structure is a functional merger of all likely alternative process topologies and process plant designs.

The evolution principle. With it, the first step is to develop a tentative, simplified version of process topology for the contemplated chemical-process system. In fact, it is an arbitrary, initial solution of the synthesis problem. As the next step, the designer modifies the plant mix and arrangement, re-adjusts the structure of process flows, and evaluates the objective function for each alternative. Then again come the analysis and optimization of the modified version, and so on, until the designer arrives at an optimal value for the system's objective function.

When one has to analyse the mathematical models of a chemical process system with a great number of dependent variables, a good deal in the development of an optimal strategy for the system's study and testing and in the choice of effective and simple computational procedures depends on the selection of a 'happy set' of optimizing independent variables.

The mathematical model of a chemical-process system includes a certain number m of system variables and parameters, or information variables. These information variables are interrelated by independent implicit functions whose number is n . As a rule, the number of information variables is in excess of the number of equations. This excess gives the number of independent variables and is referred to as the degrees of freedom, F , of the chemical-process system:

$$F = m - n$$

Thus, the degrees of freedom are the number of independent variables necessary and sufficient for a complete description of a chemical-process system's operation.

The values of some independent variables are stated in advance in the design specifications or stem from the process requirements. These are the specified variables. Some degrees of freedom are taken up by these variables. The remaining independent variables may be divided into two categories. One includes the variables assumed (or fixed) prior to calculations. The other includes the independent variables which are taken as optimizing ones — by varying their numerical values the system's operation is optimized.

Which of the independent variables are taken as optimizing ones has a vital bearing on the complexity of computational procedures in the development of a chemical-process system. It is customary to develop algorithms for the 'best' choice of optimizing independent variables. This is often done by resort to various topological models.

13.8 Layout of Plant Items

As already noted, a great number of alternative designs differing in process topology has to be tested by trial and error during the synthesis and optimization of a chemical-process system. In addition to the designer's intuition, this number can substantially be reduced through the ability to foresee or at least pre-evaluate the effect that should be expected with any one of several layouts of system elements. Hence comes the need to examine the most common layouts of plant items, to evaluate each type, to see how it will affect the quantity and quality of the product, and to decide when it should preferably be used in practice.

Despite the complexity of existing chemical-process systems, it appears feasible to identify some typical layouts of simple elements into a complete plant. Above all, any chemical processing unit may operate either continuously (continuous operation), or intermittently (batch operation), or by combination of both (semi-batch or semi-continuous operation). With continuous operation, the basic types of layout for the plant items (system elements) to make up a complete plant are as shown in Fig. 13.13. Here are (a) a series (in-line or consecutive) layout, (b) a parallel layout, (c) a layout with a bypass, (d) through (g) layouts with a recycle, and (h) a combination of those listed above. Of course, there may also be other forms of layouts for plant items.

With a *series layout* (see Fig. 13.13a), all of the process stream leaving the preceding vessel enters the next, and the stream flows through each item only once.

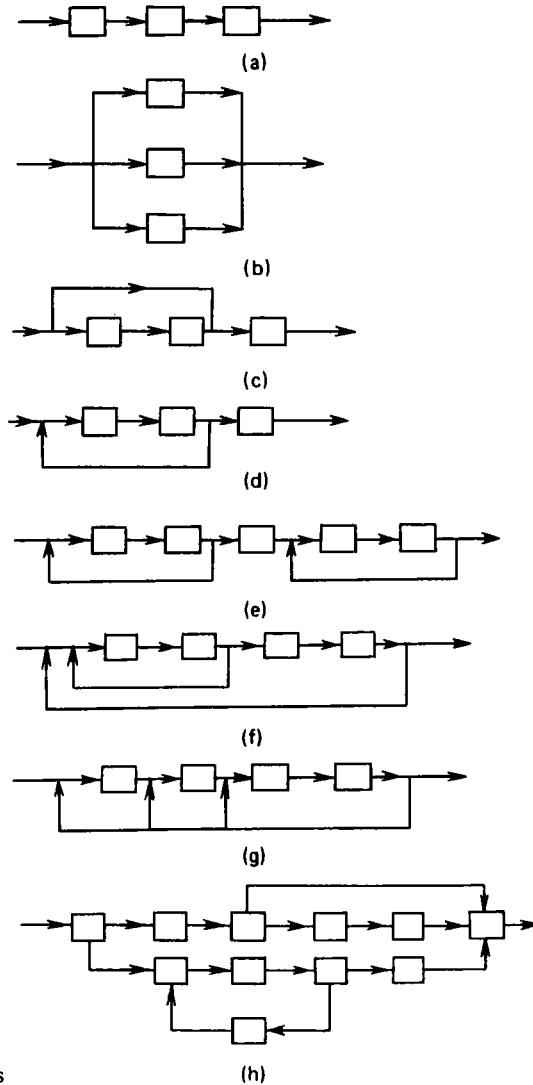


Fig. 13.13 Layout of plant items

With a *parallel layout* (see Fig. 13.13b), the feed stream is divided into several smaller streams, and these enter several system elements (plant items) at the same time. The streams leaving these elements may merge together or they may be withdrawn from the system separately. Again, a given stream passes through each plant item only once.

Before we can say when any of the two layouts — series or parallel — is more advantageous to use, let us see what effect can be gained from either arrangement of tubular and stirred-tank reactors.

A cascade of m series connected tubular reactors gives the same conversion x_A as a single tubular reactor if their respective volumes, V_{casc} and V_{single} , are the same. To demonstrate this, let us find the values of V_{single} and V_{casc} required for the same x_A to be obtained.

The volume of one tubular reactor is

$$V_{single} = vC_{A,0} \int_0^{x_A} dx_A / w_{rA} \quad (13.15)$$

The volume of any i th reactor, V_i , in a cascade is given by

$$V_i = vC_{A,0} \int_{x_{A,i-1}}^{x_{A,i}} dx_A / w_{rA} \quad (13.16)$$

The cascade includes a total of m reactors. Hence, the total volume of the cascade, V_{casc} , is

$$V_{casc} = \sum_{i=1}^m V_i = vC_{A,0} \left[\int_0^{x_{A,1}} dx_A / w_{rA} + \int_{x_{A,1}}^{x_{A,2}} dx_A / w_{rA} + \dots + \int_{x_{A,i-1}}^{x_{A,i}} dx_A / w_{rA} + \dots + \int_{x_{A,m-1}}^{x_{A,m}} dx_A / w_{rA} \right] \quad (13.17)$$

The term in square brackets in Eq. (13.17) is the sum of integrals. The upper limit of every preceding integral is the same as the lower limit of the next. This sum of integrals may be replaced with a single integral for which the lower limit is the lower limit of the first integral in the sum, and the upper limit is the upper limit of the last integral in the sum. Then the volume of a cascade of tubular reactors will be

$$V_{casc} = v \int_0^{x_A} dx_A / w_{rA} \quad (13.18)$$

It is seen from Eqs. (13.15) and (13.18) that for the same conversion to be achieved in a single tubular reactor and in a cascade of such reactors the volume must be the same in each case:

$$V_{casc} = V_{single}$$

Therefore, if and when necessary, a single tubular reactor may be replaced with a cascade of reactors having the same total volume without any risk of bringing down the conversion of the reactant because m tubular reactors of total volume V_{casc} will assure the same degree of conversion as a single tubular reactor of the same volume.

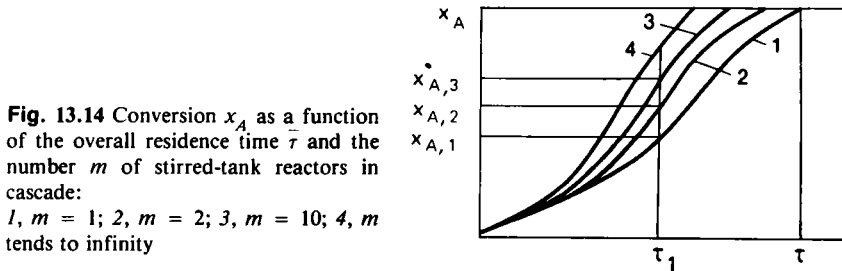


Fig. 13.14 Conversion x_A as a function of the overall residence time $\bar{\tau}$ and the number m of stirred-tank reactors in cascade:
 1, $m = 1$; 2, $m = 2$; 3, $m = 10$; 4, m tends to infinity

The series layout of stirred-tank reactors, that is, a cascade of such reactors, has already been examined (see Chap. 7). The replacement of a single stirred-tank reactor of volume V_{single} with a cascade of stirred-tank reactors of the same total volume, $V_{casc} = V_{single}$, offers an added benefit in comparison with the similar arrangement of tubular reactors. With the total volume of the cascade held constant, the conversion increases over what it is in the case of a single stirred-tank reactor and does so in proportion to the number of cascaded reactors. Figure 13.14 illustrates how the conversion x_A varies with the overall residence time $\bar{\tau}$ in a cascade (the total volume of the cascade is proportional to this quantity) for systems of a varying number m of reactors.

If we compare several cascades of stirred-tank reactors, all of the same total volume at a constant value of $\bar{\tau}_i$, we will see that the conversion increases in proportion to the number of reactors in cascade:

$$x_{A,1} < x_{A,2} < x_{A,3} \quad \text{at} \quad \bar{\tau}_i = \text{const}$$

This is because the replacement of a single stirred-tank reactor with a cascade of such reactors brings about changes in the flow pattern and the concentration distribution in the system. As the number of reactors in a cascade is increased, the two variables approach in value those associated with a tubular reactor.

Whereas with a series layout different performance is shown by stirred-tank and tubular reactors, it is the same with a parallel layout. Therefore, the findings derived below hold equally for a parallel layout of stirred-tank and tubular reactors.

With a parallel layout the total loading v is shared among m reactors. The loading sustained by each i th reactor, v_i , is

$$v_i = v/m$$

When the total volume of the system is V , that of each i th reactor is

$$V_i = V/m$$

The residence time in the i th reactor with the total loading shared as stated above,

$$\bar{\tau}_i = V_i/v_i = (V/m)/(v/m) = V/v$$

will be the same as in a single reactor of volume V and at loading v :

$$\bar{\tau} = V/v$$

For a parallel layout of tubular reactors

$$\bar{\tau}_i = \bar{\tau} = C_{A,0} \int_0^{x_A} dx_A / w_{rA}$$

For a parallel layout of stirred-tank reactors

$$\bar{\tau}_i = \bar{\tau} = C_{A,0} (x_A / w_{rA})$$

Since the division of the total feed stream into a number of parallel streams leaves the residence time unaffected, the conversion at the exit from the i th reactor will be the same as it is in a single reactor of volume V and at loading v .

Therefore, if and when necessary, one tubular (stirred-tank) reactor may be replaced with m parallel connected tubular (stirred-tank) reactors of the same total volume and at the same total loading, and this will not affect the conversion of the feed in the least.

A need to replace a single reactor with a bank of parallel or series connected reactors may arise when it is necessary to step up the overall throughput of the plant.

Among the various ways and means of enhancing the throughput of a plant, mention should be made of two:

(1) By an increase in feed loading while keeping the conversion unchanged.

(2) By an increase in the conversion of the feed (at a constant feed flow rate) by an increase in the residence time $\bar{\tau}$.

As often as not, both possibilities are exploited in practice. In each case, one has to increase the reactor volume because $V = v\bar{\tau}$.

With a tubular reactor this may require a prohibitively large reactor length because

$$L = u\bar{\tau}$$

where u is the linear velocity of the reactant stream. Here it is advantageous to replace the long reactor with a cascade of m shorter reactors. Then the length l of each i th reactor in a cascade of tubular reactors and the volume V_i of each i th reactor in a cascade of stirred-tank reactors will be reduced by a factor of m :

$$l = L/m$$

and

$$V_{i(casc)} = V/m$$

As has been shown, this will not affect the conversion in the case of a cascade of tubular reactors, and will enhance it in the case of a cascade of stirred-tank reactors.

If it is desired to increase the throughput of a plant by processing more raw materials, but the conversion should be left unchanged for one reason or another (such as when parallel reactions are effected and the order of the main reaction exceeds that of the side reaction), it is likewise necessary to increase the reactor volume V . However, this volume may well prove too large to be acceptable (with a tubular reactor it may turn out that the calculated cross-sectional area A will be prohibitively large). In such a case, it is warranted to use several reactors connected in parallel instead of a single reactor. This will leave the degree of conversion unaffected, but the cross-sectional area, a , of each i th tubular reactor and the volume, V_i , of each i th stirred-tank reactor will be reduced by a factor of m :

$$a = A / m$$

and

$$V_{i(par)} = V / m$$

Several more cases where series and parallel layouts are warranted deserve notice. A series layout is convenient where the chemical conversion is to be effected in several steps and for each step it is important to choose an optimal temperature (as in a multi-stage chemical reactor). A series layout will also be preferable so as to assure optimal temperature conditions for endothermic and exothermic reactions. Each reactor (stage) will then operate adiabatically, and an intermediate heat exchange will take place between the stages.

When an endothermic reaction is effected, the heating of the reactants between the stages allows a high rate to be maintained throughout the process. This is illustrated in Fig. 13.15 which shows how the reaction rate varies when an endothermic reaction is effected in a cascade of tubular reactors, with the reactants heated between the stages. For comparison it also shows how the reaction rate would vary if the process were effected in a single reactor and if there were no reactant heating between the stages.

With reversible exothermic reactions, too, it is widely practised to connect reactors (or the stages of a reactor) in series, with heat withdrawn between the stages so as to maintain the process temperature at an optimal

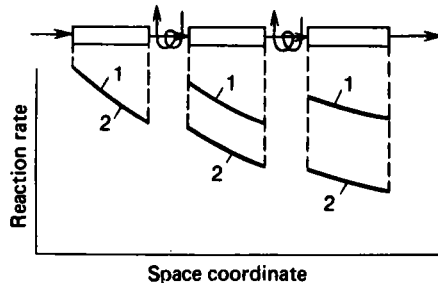


Fig. 13.15 Changes in reaction rate in a cascade of tubular reactors:
1, with reactants re-heated between stages; 2, without re-heating between stages

value. Many examples of how this is done were given in Chap. 10 to demonstrate practical methods for assuring an optimal process temperature. Again it is to be stressed that a series arrangement may be used both in a system of reactors and inside a single reactor.

Still other examples of series layout are a cascade of separation units with an optimal degree of separation maintained in each unit, a multistage compressor with an optimal pressure drop maintained across each stage, etc.

Apart from the cases cited earlier, a parallel layout is employed when it is important to share the loading in an optimal way among several units which include plant items differing in performance for some reasons (because of a contaminated heat-exchange surface, an exhausted catalyst, etc.), although they may well have been built to have the same design capacity.

A parallel layout is likewise advantageous when the same feedstock is used to obtain two or more intermediates which then go to make a single end product.

A *layout with a bypass* is a series connection of plant items through which only some of the total process stream entering the system is allowed to pass. The remainder of the feed stream is routed round one or several plant items and then merges with the main body of the stream (Fig. 13.16). The stream q_1 entering the system is called the forward stream. It divides into two parts. One part, q_2 , is passed through the plant items. This is the main stream; it controls the course of the process in the reactors. The other part, q_3 , is routed round the reactors and ultimately joins the main stream. This is a bypass stream. In the reactor layout with a bypass, the two streams flow in the same direction, and each stream passes through any pieces of plant only once.

With a bypass layout, the residence time of the reactants is increased and the reactant conversion is enhanced because the quantity of feed in the main stream (the one passing through the reactor) is decreased.

Bypassing is widely used to assure optimal temperature conditions for reversible exothermic reactions (see Fig. 10.26). As will be recalled, there is a need, in the case of such reactions, to bring down the process temperature from reactor to reactor or from one stage to the next. Bypassing solves this problem. The main stream passing through the reactor is heated due to the exothermic reaction that is effected there and leaves the vessel hot. Before it enters the next reactor or stage, this stream must be cooled. This is done

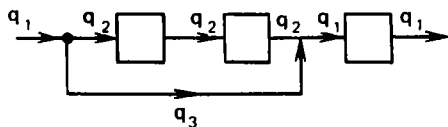


Fig. 13.16 Layout with a bypass

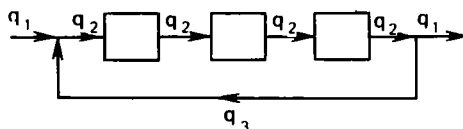


Fig. 13.17 Layout with a recycle

by adding the cold bypass stream to the hot main stream in such a way that an optimal temperature is obtained at the inlet to the next reactor.

Bypassing has one more beneficial effect on the system. The bypass stream does not undergo a chemical conversion and carries the reactant in a high concentration. Mixing together the bypass and main streams assures a high reactant concentration exactly at the temperature that is optimal at the inlet to the next reactor.

A *layout with a recycle* has at least one backward-directed stream in a series connection of process elements (Fig. 13.17). The backward stream, or recycle, connects the exit of an element down the stream to the inlet of an element upstream. This latter element may be located next to the former one, or they may be spaced several stages apart.

In contrast to the series, parallel and bypass layouts, all of which fall in the category of open-circuit systems, a layout with a recycle belongs to closed-circuit systems — the recycle from a reactor downstream to one or several reactors upstream is in effect feedback and thus forms a closed-circuit subsystem (a closed loop) of a chemical-process system.

The stream, q_1 (see Fig. 13.17), entering the system is termed the forward stream. The stream q_2 passing through the plant items and controlling their operating conditions is referred to as the main stream, and the stream q_3 which arises when the main stream divides at the exit from a reactor and flows back to the inlet to the closed circuit is called the recycled stream.

Operation of a layout with a recycle may be described in terms of the recycle ratio R or the recycle coefficient K_r . The recycle ratio R defines the fraction of the main stream that is recycled:

$$R = \frac{\text{Recycle stream}}{\text{Main stream}} = q_3 / q_2 \quad (13.19)$$

The recycle coefficient K_r shows how many times the main stream is greater than the forward stream:

$$K_r = \frac{\text{Main stream}}{\text{Forward stream}} = q_2 / q_1 \quad (13.20)$$

Since

$$q_2 = q_1 + q_3$$

it is seen that R and K_r are interconnected by the following relations:

$$R = 1 - 1/K_r \quad (13.21)$$

$$K_r = 1/(1 - R) \quad (13.22)$$

Recycling offers a solution to many important process problems, thereby enhancing the performance of chemical-process systems. Above all, it helps utilize the raw material to the utmost in reactors where the conversion would otherwise be incomplete. As will be recalled, the reaction rate falls abruptly as the equilibrium condition is approached. Indeed, it often happens in practice that the process has to be interrupted well before the equilibrium is attained, and so a complete conversion cannot be assured. The situation is especially aggravated when the state of equilibrium is unfavourable — the equilibrium content of the product is low. In the circumstances, the process will terminate far away from complete conversion.

Recycling goes a long way towards assuring a high degree of conversion. The main reactant stream leaving the reactor carries a small proportion of the product; this product is withdrawn, and the unreacted material is returned as a recycle to the reactor for a further conversion. As a result, more of the raw material is further reacted to give a higher overall conversion.

Importantly, recycling is the only way to enhance reactant conversion when other known methods (manipulation of temperature, pressure, component concentration, etc.) have been fully exhausted but failed to give the desired result. An instructive example is ammonia manufacture.

The withdrawal of the product from the feed stream in processes with a recycle has one more positive effect — it avoids a reduction in the reactant concentration due to the dilution by the products. As a result, the process rate can be maintained at a high value, and this provides for an increase in its driving force.

There are processes in which a high degree of conversion could be obtained from thermodynamic considerations, but it is undesirable due to some other motives. A situation like that often happens in organic syntheses involving complex reactions. As often as not, an increase in conversion might entail a decrease in the selectivity of the process, so it appears more attractive to effect it at low levels of conversion. This can be done with recycling — the reactor will provide for a low degree of conversion, but a high overall conversion will be obtained by recycling the unreacted stock back to the reactor. Recycling can give a high overall yield for any product of a complex reaction, which is not always the case when traditional methods of reaction control are employed.

In many processes it is convenient to effect the chemical conversion with an excess of a reactant. After the chemical change the excess remains unused, and it may be recycled to the process to advantage.

In the main, the principal objective of recycling is to enhance the

utilization of the raw material. This is accompanied by improvement in the utilization of plant as well. At the same time, recycling provides for a better use of the system's energy resources (because the difference in heat put into and withdrawn from the system with products is reduced to a minimum), and for better operating conditions of the system, such as temperature, reactant concentration, and residence time.

Recycling comes into the picture where one has to regenerate a multitude of auxiliary agents used in industrial chemical processes, such as solvents, adsorbents, catalysts, etc.

Figure 13.17 shows the simplest case of recycle. Industrial practice uses many other modifications of layout with a recycle (see Fig. 13.13). Thus, a system may have several recycle loops; the recycle may be carried to several vessels rather than to one; sometimes these plant items may belong to different processes or one and the same vessel may receive recycles from different plant items (variously called as conjugate, distributed and hybrid recycles).

Recycling is widely used in many present-day chemical processes, such as the manufacture of ammonia, soda, methanol, and ethanol. The reason is this: an exhaustively complete conversion is obtained, the yield of by-products is held to minimum, and the reactions are effected at a high rate. All this contributes to a maximum utilization per unit volume of reactor.

13.9 Technological Principles Underlying the Development of Chemical-Process Systems

The tasks facing the designer at all levels, that is, in the analysis, synthesis and optimization of a chemical-process system, development of new high-performance chemical enterprises, intensification and optimization of existing chemical complexes, must all be tackled on the basis of a precisely formulated objective function.

The objective function should be chosen and the conditions for its optimization should be assured in the light of the advanced technological principles underlying the development of chemical-process systems. These include rational use of raw materials and energy, use of bigger plant items and units, reduction of production wastes, control of objectionable emissions and effluents from chemical processing, establishment of low-waste or wasteless manufactures, etc. When properly adhered to, these principles will enable the designer to come up with a processing unit which shows optimal performance both technically and economically.

Practically, these principles are embodied in concrete measures and activities aimed at achieving the above tasks. These measures and activities have already been discussed in the text, so the reader is already acquainted with them. It only remains to summarize what he has learned.

Rational use of raw materials. This is assured through the following:

- (1) The raw materials should be processed to the utmost.
- (2) All values should be recovered from a raw material.
- (3) The quantity of production wastes must be minimized.

In practice, this can be done through a proper choice of process layout, the use of one of the reactants in excess, feeding the reactants in countercurrent, recycling, reactant regeneration, etc.

Rational use of energy. This is implemented by several techniques, such as waste heat recovery, optimal heat exchange in reactors, and power cogeneration. Waste heat recovery helps minimize the expenditure of heat and other forms of energy, while power cogeneration makes the utmost use of the raw materials' energy potential.

Use of pieces of equipment of a large unit capacity. This is among the most promising trends in present-day industrial chemistry as it offers quite a number of advantages.

Control of objectionable emissions and effluents from chemical processing. No high-performance chemical processing unit can be built without a proper protection of the biosphere against various emissions. This task is being handled in two directions, as follows.

(1) Methods are being developed to decontaminate and reclaim the wastes, emissions and effluents from existing chemical complexes.

(2) Processes themselves are being perfected so as to minimize industrial wastes, and low-waste and wasteless manufactures are being set up, working their raw materials so as to recover all of their values and operating closed-circuit.

13.10 Problems Arising in the Development and Operation of Plant of Large Unit Capacity

Recent decades have seen an impressive increase in the unit capacity of plant, especially in the manufacture of fertilizers, pesticides, chemical fibres, and plastics. A very instructive example of this trend is offered by ammonia manufacture. Thus, the unit capacity of ammonia synthesis plants increased from 25-30 thousand tonnes per year in 1959-1965 to 50-100 thousand tonnes in 1966-1970, and to 450 thousand tonnes in 1981-1983. Design work is under way on a unit of as much as 800 thousand tonnes of ammonia per year.

The same trend has prevailed in the manufacture of other products. At this writing the unit capacity of processing plant (in thousand tonnes per year) is as follows:

Ammonium nitrate	450
Sulphuric acid	500

Phosphoric acid	300
Ammonium phosphate fertilizer	131
NPK fertilizer (Nitrophoska type)	112
NPK fertilizer (Nitroammophoska type)	136

The production of phosphorous fertilizers is given in terms of P_2O_5 .

There has been a sizeable increase in the unit capacity of plant in the manufacture of ethylene, propylene, benzene, toluene, xylenes, butadiene, and paraffins, all of them essential for the manufacture of plastics, synthetic elastomers, chemical fibres, film materials, surfactants, detergents, and other products.

The increase in unit capacity is one of the most important activities which have as their objective to reduce capital and operating costs, labour requirements, and manufacturing costs, and to simplify process control and management.

With plant of a large unit capacity, the return on investment is increased due to the following factors:

(1) The consumption of raw materials per unit of product is independent of plant capacity.

(2) The energy required to make up for the lost heat is proportional to $(M_2/M_1)^{1/2}$, rather than to M_2/M_1 , where M_1 is the capacity of a conventional unit-size plant and M_2 is that of a larger unit size. In other words, the specific energy consumption decreases with increasing unit capacity.

(3) The specific capital costs are reduced. When the unit capacity is doubled, the specific capital costs are cut down by 15-20%.

(4) The total cost of plant increases as the power $z = 0.6$ to 1, rather than in direct proportion to the unit capacity:

$$K_2 M_2 / K_1 M_1 = (M_2 / M_1)^z \quad (13.23)$$

where K_1 is the capital costs of a conventional unit-size plant and K_2 is that of plant of a large unit capacity.

(5) The manufacturing cost of the product decreases with increasing unit capacity:

$$S_2 / S_1 = (M_1 / M_2)^n \quad (13.24)$$

where:

S_1 = manufacturing cost of the product in a conventional unit-size plant

S_2 = manufacturing cost of the product in a plant of a large unit capacity

n = 0.2 to 0.3

When the unit capacity is doubled, the manufacturing cost is cut down by 13-15%.

As is seen, unit capacity may be increased only within certain technical and economic bounds. On the technical side, these bounds stem from the complexity of structural design, erection and operation and the reliability of large-capacity plant items. On the economic side, the bounds on unit capacity are set by the likely loss of product in the case of plant shutdown in an emergency or some failure. Even a short-duration shutdown of a large-capacity plant unit might have an adverse effect on product output and give rise to wider repercussions.

Also, when a large-capacity plant unit is purged, the instantaneous emissions can negatively affect the biosphere to a far greater extent than emissions from smaller plant items.

An optimal unit capacity depends on the state of the art and the demand for the product. Unit capacity may be increased by building items of larger size while retaining the technological principles underlying the processing of raw materials, or it may be increased through a greater specific throughput on the basis of novel processing principles and by extending the time in operation per year owing to higher plant reliability.

The increase in the overall size of a plant item poses technical problems: bigger pieces are far more difficult to fabricate, transport, erect and repair. Therefore, the approach of choice is to build large-capacity plant items and units that embody novel technological ideas. For example, when sulphuric acid is manufactured at a pressure of 0.5-0.6 MPa, the plant's area is one-fourth of what it is when the process is effected at atmospheric pressure, and the requirements for metalwork are cut down to one-third. Plans are afoot in the USSR to build a cyclic sulphuric-acid plant whose capacity will be 600-800 thousand tonnes per year. It will operate at a pressure of 1.5 MPa and use oxygen for process purposes. This will be a practically wasteless plant.

On the other hand, it does not pay to use plant of large unit capacity in the manufacture of a wide range of products close in composition and in the functions performed (such as extrapure substances, cine and photographic materials, pesticides, synthetic detergents, dyes, fibres, paints and varnishes, etc.). Their production can better be expanded through the use of flexible manufacturing systems (FMSs). Incorporating automated work cells or work centres, they can readily be re-adapted to synthesize a broad gamut of chemical products. A chemical processing unit set up as an FMS is in effect an assemblage of mixers, reactors, coolers, tanks, weighers, pumps and other plant items which may be re-configured into any layout best suited to a given synthesis.

Fundamentally new types of high-performance process equipment assuring rational use of raw materials, fuels, energy and labour, and proper environmental pollution control can only be developed from in-depth

studies of, and reliance on, the latest advances in science and technology, especially in the theory of chemical engineering, the physics and chemistry of heterogeneous systems, the physics and engineering of energy generation, mechanics and mechanical engineering, economics, computer engineering, computer control and management.

Part Four

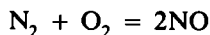
PRACTICAL APPLICATIONS OF CHEMICAL ENGINEERING

Chapter Fourteen

FIXED NITROGEN TECHNOLOGY

Gaseous nitrogen is among the most stable chemical substances. The chemical bond energy in a nitrogen molecule is 945 kJ mol^{-1} . Since it has a very high entropy per atom, elemental nitrogen is highly nonreactive. In the atmosphere nitrogen is present in a free state and in large quantities. It has been calculated that the air blanket over every hectare of the Earth's surface contains about 80 thousand tonnes of nitrogen. Elemental nitrogen accumulated by the bacteria thriving on the roots of some plants reacts with the formation of amino acids and proteins. This reaction is catalysed by enzymes, and the necessary energy is supplied by photosynthesis.

Some nitrogen is converted to a biologically assimilable form by lightning discharges according to the scheme



Most organisms readily assimilate nitrogen compounds whose negative oxidation state is -3 . These are alpha-amino acids answering the general formula $\text{RCHNH}_2\text{COOH}$ and their polymers — proteins which play an extremely important role in biochemistry. However, the transition to an oxidation state of -3 under natural conditions is too slow to maintain the requisite supply of fixed nitrogen at existing uptake rates.

On average, half the nitrogen required to support life processes comes back through the atmosphere in 10^8 years. For oxygen this cycle takes 3000 years to complete, and for carbon, 100 years. These figures are a convincing argument in favour of synthesis of nitrogen-bearing compounds assimilable by living organisms.

The leading consumers of nitrogen compounds have long been pharmaceuticals, the military, and industry. In the early 19th century they were joined by agriculture.

The problem of industrial nitrogen fixation was solved with the advent of ammonia synthesis. Since it was first commercialized, a vast supply of feedstocks has been developed for the production of a great variety of nitrogen-bearing compounds.

14.1 Raw Materials for the Nitrogen Industry

The raw materials for the nitrogen industry are atmospheric air and various fuels. As a chemical raw material, air has been described in Chap. 11. One of its constituent gases is nitrogen which is used in the manufacture of ammonia, calcium cyanamide, and some other products of nitrogen technology. In some ammonia synthesis schemes, nitrogen need not be separated from air in pure form; air is added to the feed gas so that the N_2 and H_2 constituents are in a stoichiometric ratio of 1:3. Other production schemes also use pure liquefied nitrogen for removal of objectionable impurities from the synthesis gas, or gaseous nitrogen which is precisely metered to the reformed gas. In the latter case, air is separated into its constituent gases by a cryogenic process.

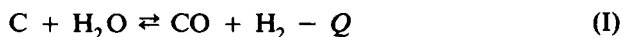
In view of the huge resources of atmospheric nitrogen, the limiting factor with regard to the supply of feedstocks for the nitrogen industry is primarily fuel — the second most important raw material used to produce hydrogen or hydrogen-bearing gases. Taking the Soviet Union as an example, prior to the 50s this was mainly solid fuel. Changes in the pattern of raw materials used in ammonia synthesis in the USSR are shown in Table 14.1.

Table 14.1 Pattern of Raw Materials for Ammonia Synthesis in the Soviet Union

Raw material	Percentage by year				
	1960	1965	1970	1975	1980
Solid fuel (coal, coke)	32.0	15.9	10.4	5.7	1.5
Coke-oven gas	32.1	18.2	14.2	11.7	5.3
Natural and refinery reforming off-gases	16.3	59.9	72.3	79.6	92.2
Others	19.3	6.0	3.1	3.0	1.0

14.2 Production of Feed Gases

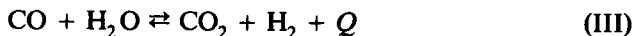
Synthesis gas from solid fuels. Originally, synthesis gas was mainly produced from solid fuel processed in water gas generators according to the reactions



In the above process, air and steam are alternately blown through a bed of coarse lumps of solid fuel (anthracite coal, coke, or semi-coke). Synthesis gas is formed at the steam-blow step, and the required temperature of the fuel bed is achieved during the air-blow step. The operating cycle of

the generator lasts 3 to 5 min. The water gas thus produced is 50-53% H_2 and about 36% CO .

Before it may be used in the subsequent production steps, the water gas must be purified to remove sulphur compounds and the carbon monoxide must be converted according to the scheme*



Following that, the carbon dioxide must be removed fully if it is to be used in ammonia synthesis, or partly if it is to be used in methanol synthesis.

Among the demerits of the process are intermittent operation, low unit throughput of the gas generator, and tight requirements for the feedstock as regards its ash content and melting point, its grain size analysis, and other characteristics.

Other processes have been tested on an industrial scale in which the gasification is effected in a fluidized bed of fine-grained fuel. A further step has been gasification in a fluidized-bed with a steam-oxygen blast applied under pressure. Tests on brown coals have yielded synthesis gas whose composition in percent by volume is this: CO_2 , 29.7; O_2 , 0.2; CO , 20.2; H_2 , 42.3; CH_4 , 7.0; and N_2 , 0.6.

Another approach is based on the gasification of a pulverized fuel. This process is applicable to practically any solid fuel. Its salient features are high turbulence in the reaction zone due to the admission of feedstock streams in countercurrent, and an intimate mixing of the steam-oxygen blast with the pulverized fuel.

Synthesis gas from liquid hydrocarbons. The production of synthesis gas from liquid hydrocarbons is widely practised in countries where the reserves of natural gas are limited. Examples are Japan and West Germany where 67% and 59% of the total ammonia was produced in 1974 from liquid fuels. Obviously, liquid fuels are as important as feedstocks for methanol production under similar conditions.

According to the manner in which synthesis gas is produced, liquid fuels may be classed into two groups. One group includes fuels processed by way of high-temperature oxygen conversion. Among them are heavy petroleum residuum, cracking bottoms and other heavy liquid fuels. The other group includes light straightrun distillates (such as naphtha) whose final boiling point is not over 200-220 °C. Among them are gasoline, naphtha, and blends of light distillates. The second group of liquid fuels is processed into synthesis gas by way of catalytic conversion with steam (steam reforming) in tubular furnace-type reactors, or reformers.

In some cases the high-temperature oxygen conversion of liquid fuels (partial combustion processes) is effected with the liquid fuel passed under

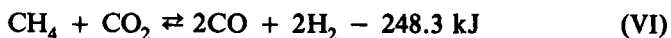
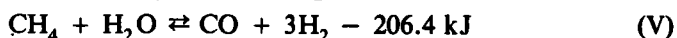
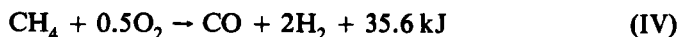
* This is known as the water-gas shift reaction. — *Translator's note.*

pressure through a preheater which it leaves at a temperature of 400-600 °C and enters a gas generator also fed with preheated oxygen and superheated steam. Synthesis gas is formed in the reactor at temperatures in the range 1350-1450 °C, but this also produces an amount of carbon black. The carbon black is removed from the gas which is then desulphurized. Following that, the gas which carries 3-5% CO₂, 45-48% CO, 40-45% H₂, and some methane, nitrogen and argon is subjected to a CO shift and treated for CO₂ removal. The process is effected at a pressure of as high as 15 MPa. The throughput of the equipment is 30 thousand m³ hr⁻¹ and more of the H₂ + CO mixture. Among the drawbacks of the process are high oxygen consumption, carbon black formation, and a complex production route.

Where synthesis gas is obtained from low-boiling-point liquid fuels by steam reforming — catalytic steam conversion in tubular reactors — the liquid fuel is first vaporized and thoroughly treated to remove all impurities. For the feedstock to qualify for the subsequent processing, its sulphur compound content ought not to exceed 1 mg per kilogram of hydrocarbons. Following that, the hydrocarbon vapour is mixed with superheated steam and fed into the reaction tubes filled with a nickel catalyst. Among the merits of this process developed in the 1960s and still widely practised in some countries are provisions for the production of synthesis gas under pressure, ease of synthesis gas composition control, and low electric power requirements. On the demerit side are stringent requirements for the composition of the feedstock in terms of unsaturated and cyclic hydrocarbons, sulphur and other impurities and a high specific consumption of hydrocarbons.

Synthesis gas from natural gas. Synthesis gas produced from hydrocarbon gases (natural gas, associated petroleum gas, fuel-processing gases) is at present the primary source for the production of ammonia and methanol. In terms of the oxidant used and the manner in which the process is carried out, the following processes may be named for the production of hydrogen-bearing gases: via partial combustion (high-temperature oxygen conversion); via steam reforming (catalytic steam-oxygen conversion) in shaft reactors and catalytic steam-CO₂ reforming in tubular reactors.

In the production of synthesis gas, the methane (which is the primary component of hydrocarbon gases) is oxidized according to the following overall reactions:



At the same time the water-gas shift reaction, (III), takes place.

Similar reaction schemes apply when the methane homologues are oxidized.

Under industrial-scale conditions, reactions (III), (V) and (VI) are reversible. The equilibrium constant of reaction (IV) over the operating temperature range is rather high, being in excess of 10^{11} . In other words, it may be deemed that the reaction proceeds to the right to completion (all of the oxygen is used up in the reaction).

Reactions (IV) through (VI) proceed with an increase in volume. Since the operations (purification of the reformed gas and synthesis) following the methane reforming step should preferably be effected at an elevated pressure, it is likewise advantageous to carry out the methane reforming likewise under pressure as this cuts down the cost of gas compression.

The reformed gas is to meet certain requirements with regard to its composition. It is characterized by the stoichiometric conversion factor s which differs from case to case and is as given in the table below.

Hydrogen	$(\text{H}_2 + \text{CO}) : (\text{CH}_4 + \text{CO}_2)$	5.5-10.0
Ammonia	$(\text{H}_2 + \text{CO}) : \text{N}_2$	3.05-3.10
Methanol	$(\text{H}_2 + \text{CO}) : (\text{CO}_2 + \text{H}_2\text{O})$	2.0-2.2
Higher alcohols	$\text{H}_2 : \text{CO}$	0.7-1.0
Substitute natural gas (SNG)	$\text{H}_2 : \text{CH}_4$	0.07-0.30

Despite the variability in the requirements that the reformed gas is expected to meet, all of its modifications can be produced by the catalytic conversion (reforming) of hydrocarbons with steam, CO_2 , oxygen, and air.

The various steps involved in the production of synthesis gas by existing plants in the nitrogen industry are shown in the flowsheet of Fig. 14.1.

Desulphurization of natural gas. Sulphur compounds are objectionable impurities in the process gas. For one thing, they are strong catalyst poisons. For another, they cause heavy corrosion to the pieces of equipment.

Natural gas from some deposits carries appreciable quantities of sulphur compounds, both inorganic and organic. The sole representative of inorganic compounds is hydrogen sulphide. The organic sulphur compounds present in natural gas are many and diverse. They include carbon oxysulphide COS, carbon disulphide CS_2 , thiophene $\text{C}_4\text{H}_4\text{S}$, sulphides R_2S , disulphides R_2S_2 , and mercaptanes RSH (methyl mercaptane CH_3SH , ethyl mercaptane $\text{C}_2\text{H}_5\text{SH}$, heavy mercaptanes such as $\text{C}_6\text{H}_5\text{SH}$).

Numerous studies have revealed that removal of a compound from the gas becomes increasingly more difficult as its molecular mass increases. The organic sulphur compound that is the hardest of all to remove is thiophene. Sulphides, disulphides and heavy mercaptanes are also difficult to remove.

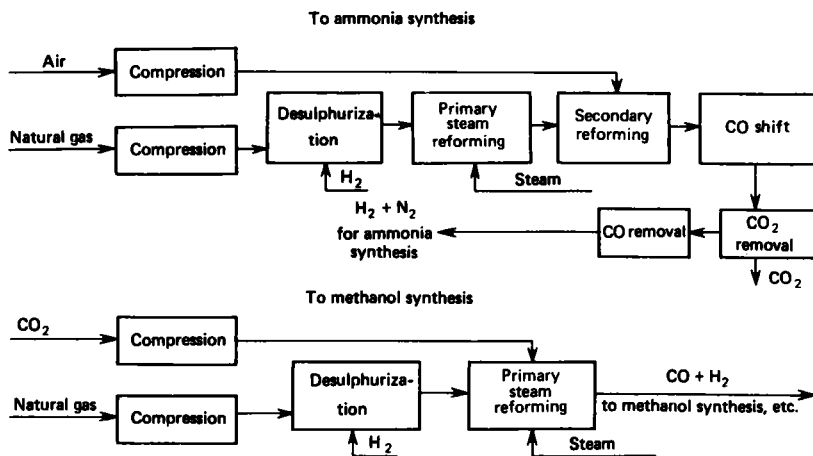
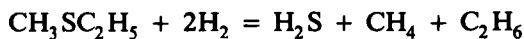
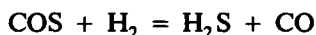
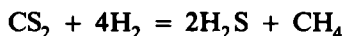
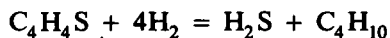
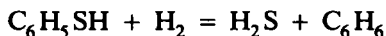
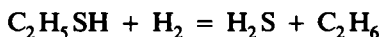


Fig. 14.1 Manufacture of synthesis gas

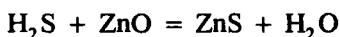
Since natural gas carries many times more heavy mercaptanes, sulphides and disulphides than it is permitted to have at entry to the reformer (1 mg m^{-3}), existing large-capacity ammonia synthesis units resort to two stages of desulphurization.

During the first stage, the organic sulphur compounds are hydrogenated over an Al-Co-Mo or Al-Ni-Mo catalyst at a temperature of $350\text{--}400^\circ\text{C}$ and a pressure of $2\text{--}4 \text{ MPa}$. The following reactions take place during the hydrogenation step:



Under the actual process conditions the above reactions may be regarded as irreversible — the hydrogenation is practically complete.

During the second stage, the hydrogen sulphide at $390\text{--}410^\circ\text{C}$ is taken up by a zinc oxide absorbent:



In the temperature range of $200\text{--}500^\circ\text{C}$ the reaction is practically irreversible and can provide for a very high degree of gas purification.

When sulphur compounds are present in increased quantities, the natural gas is purified by an adsorption method employing synthetic

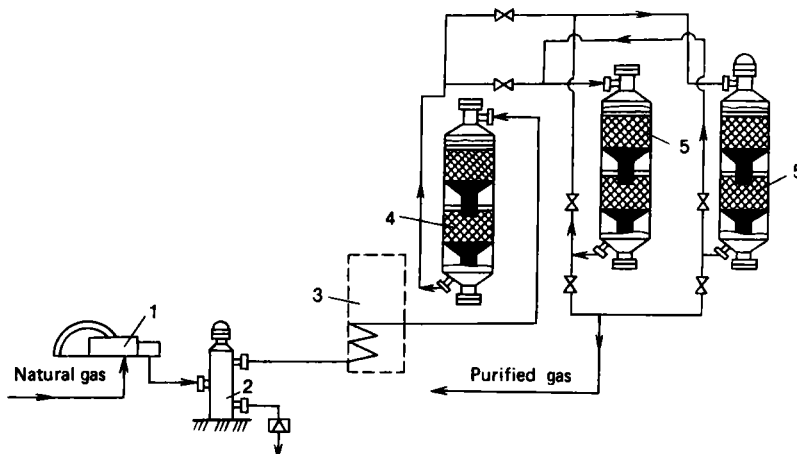


Fig. 14.2 Flowsheet for two-stage purification of natural gas:
1, gas compressor; 2, separator; 3, preheater; 4, desulphurizer; 5, zinc adsorber

zeolites (molecular sieves). The zeolite of choice is one made up of Na_2O , Al_2O_3 , and SiO_2 . The sorption is effected at nearly room temperature. The zeolites are regenerated at a temperature of 300–400 °C, using either nitrogen or a purified gas and gradually raising the temperature. The bulk of the sulphur (65%) is given off at 120–200 °C.

Sulphur removal may be carried out in radial, shelf or shaft desulphurizers. Figure 14.2 shows a flowsheet for sulphur removal from natural gas in two stages in shelf adsorbers.

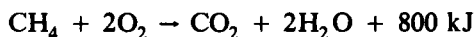
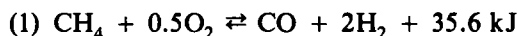
Steam reforming. The equilibrium composition of the resultant gas mixture is determined by process variables such as the temperature and pressure in the system and the ratio of the reacting components. As has been noted, steam reforming may be described by Reaction (V).

Given atmospheric pressure and the stoichiometric ratio of the feed components, a sufficiently complete conversion of the methane takes place at temperatures around 800 °C. The same degree of methane reforming can be achieved at lower temperatures but at higher steam flow rates. Pressure markedly reduces the degree of conversion. At 3 MPa, for example, a sufficiently complete conversion will take place at temperatures close to 1100 °C.

In existing units operating at 2 MPa and higher and at a 1:4 methane-steam ratio, the methane content after steam reforming is 8 to 10% by volume. So as to keep the residual methane content to about 0.5% by volume, the reforming operation is effected in two steps. The first step is steam reforming under pressure, and the second step is steam-air reforming using atmospheric oxygen. This produces synthesis gas of a stoichiometric

composition and there is no need to separate air for the production of process oxygen and nitrogen.

Partial combustion of methane with oxygen. To yield hydrogen, the process should be carried out so that the methane is oxidized incompletely. The reaction proceeds in two steps:



The equilibrium constants of the first step are so high that the reactions may be deemed practically irreversible. Therefore, an increase in the oxygen concentration in the feed gas over its stoichiometric value does not lead to an increase in the yield.

As with steam reforming, an increase in pressure during the partial combustion is not warranted thermodynamically. A high degree of conversion for methane at elevated pressure can be assured by carrying out the process at higher temperatures.

The steam reforming and partial combustion processes discussed above differ in the thermal effect they produce. The steam reforming reactions are endothermic, so they call for heat input. The partial combustion reactions are exothermic, so the heat they evolve is enough not only for the partial combustion proper to proceed autothermally, but also to sustain the endothermic reactions of steam reforming. Therefore it is advantageous to effect methane reforming by a combination of oxidants.

Steam-oxygen, steam-oxygen-air and steam-air processes. An autothermal process (the one without heat input from external sources) can be effected by combining exothermic reaction (IV) and endothermic reaction (V). It may be referred to as the steam-oxygen process if the oxidants are steam and oxygen, or as the steam-oxygen-air process if the oxidants are steam, oxygen, and air.

The two processes have found wide use in industrial practice. The steam-oxygen process yields a nitrogen-free reformed gas. The steam-oxygen-air process produces a reformed gas which carries nitrogen in an amount needed to obtain a stoichiometric $\text{H}_2 + \text{N}_2$ mixture for ammonia synthesis, that is, 75% H_2 and 25% N_2 .

The plot in Fig. 14.3 illustrates how the addition and excess of steam affects the minimum temperature required for the production of synthesis gas which has a stoichiometric composition and carries 0.5% by volume residual methane. In the pressure range of 1-4 MPa, doubling the steam to methane ratio enables the reforming temperature to be brought down by 55-60 deg. C.

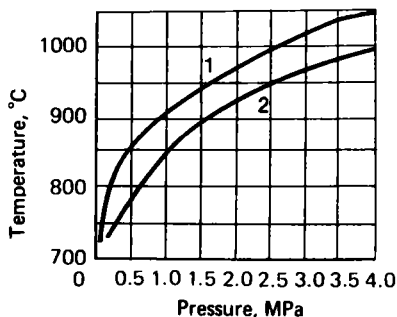
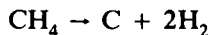


Fig. 14.3 Minimum required temperature of ammonia synthesis gas production as a function of pressure:

1, at a 1:2 CH₄/H₂O ratio; 2, at a 1:4 CH₄/H₂O ratio

Methane reforming catalysts. Without a catalyst, methane reacts with steam and carbon dioxide at an extremely slow rate. Under industrial-scale conditions, the process is effected over catalysts. Apart from substantially speeding up the reforming reactions, they serve, in the presence of an appropriate excess of oxidants, to avoid the reaction



Catalysts differ from one another not only in the active component content, but also in appearance and the percentage of base material and promoters.

In the above process, the best catalytic effect is produced by nickel catalysts with alumina, Al₂O₃, as the base material. The nickel catalysts to be used in methane reforming come as pellets or extruded Raschig rings. Their composition is this: NiO, 25%; Al₂O₃, 57%; CaO, 10%; and MgO, 8%.

When properly used, reforming catalysts may last in service for three years or even more. Their activity can be impaired by various catalyst poisons. Nickel catalysts are most sensitive to sulphur compounds. Poisoning occurs as the catalyst's surface is covered with nickel sulphides entirely inert towards the conversion of methane and of its homologues. A sulphur-poisoned catalyst can be regenerated nearly completely by feeding a pure gas at a certain temperature into the reformer. The activity of a carburized catalyst can be restored by treating it with steam.

Carbon monoxide shift. This is effected according to Reaction (III). As has been shown, this reaction takes place in part already at the steam reforming step, but the conversion of the carbon monoxide is low and the exit gas carries as much as 11.0 vol. % CO or even more. As a way of obtaining an additional quantity of hydrogen and keeping the carbon monoxide content of the reformed gas to a minimum, it is customary to effect the carbon monoxide shift as an independent reaction.

In agreement with the conditions for thermodynamic equilibrium, the conversion of carbon monoxide to carbon dioxide and hydrogen with

steam can be enhanced by removing the carbon dioxide from the raw synthesis gas, raising the steam content, or effecting the process at the lowest possible temperature. As is seen from the reaction equation, the CO shift does not entail an increase in volume. Therefore, an increase in pressure does not shift the equilibrium position. At the same time, it is economically advantageous to effect the shift operation at an elevated pressure because the reaction rate is increased, the required vessel size is decreased, and the energy of the previously compressed natural gas is better utilized.

The carbon monoxide shift operation with an interstage withdrawal of carbon dioxide is employed in the production of hydrogen when the latter is to carry as little methane as practicable.

The steam content of the raw synthesis gas is usually due to the steam introduced for methane reforming and that remaining subsequently. The steam-to-gas ratio before the CO shift in large ammonia synthesis units is 4 or 5 to 10. Carrying out the operation at low temperatures is an effective way of raising the equilibrium conversion of the carbon monoxide, but it is possible only in the presence of highly active catalysts. It is to be noted that the temperature cannot be brought down below a certain limit because of the likely steam condensation. When the shift operation is effected at a pressure of 2 or 3 MPa, this limit is 180-200 °C. If the temperature were allowed to fall below the dew point, the moisture would condense on the catalyst, and this is an objectionable development.

The CO shift is accompanied by the evolution of a considerable quantity of heat. Because of this, the operation is usually effected in two steps, each step at a temperature of its own. The high temperature maintained during the first step provides for a high rate of conversion of a large quantity of carbon monoxide. The reduced temperature maintained during the second step provides for a high degree of conversion of the remaining CO. The heat of the exothermic reaction is reclaimed to raise steam. In this way, the desired conversion is achieved along with a reduction in steam consumption.

The temperature to be maintained at each step depends on the properties of the catalysts used. The first step uses an iron-chromium catalyst available as pellets and shapes. Industrially, use is made of a medium-temperature iron-chromium catalyst.

The poisons effective against the iron-chromium catalyst are sulphur compounds. Hydrogen sulphide reacts with Fe_3O_4 to form iron sulphide, FeS . Organic sulphur compounds react, in the presence of an iron-chromium catalyst, to form hydrogen sulphide. Apart from sulphur compounds, the iron-chromium catalyst may be poisoned by compounds of phosphorus, boron, silicon, and chlorine.

The low-temperature shift catalysts contain compounds of copper, zinc, aluminium and, sometimes, chromium. Two-, three-, four-, and

multi-component catalysts are known to have been developed. The additives to the above listed elements may be compounds of magnesium, titanium, palladium, manganese, cobalt and some other elements. The copper content of the catalysts ranges between 20 and 50% (in terms of the oxide). Owing to the addition of aluminium, magnesium and manganese compounds to these catalysts, they are more stable towards any rise in temperature and other factors.

Prior to use, a low-temperature shift-reaction catalyst is reduced with carbon monoxide or hydrogen. This treatment forms its active surface. The copper oxide and other copper compounds are reduced with the formation of finely dispersed metallic copper which, in the opinion of many investigators, enhances the catalytic activity.

The service life of low-temperature shift catalysts does not usually exceed two years. One reason why catalysts lose their activity is recrystallization under the influence of temperature and the feedstock. As moisture condenses on a catalyst, it loses some of its mechanical strength and activity. The loss of mechanical strength results in the destruction of the catalyst and is accompanied by an increase in the pressure drop across the reactor. Compounds of sulphur and chlorine, unsaturated hydrocarbons and ammonia poison the low-temperature shift catalysts. The concentration of hydrogen sulphide in the feedstock ought not to exceed 0.5 mg m^{-3} .

Plant types for synthesis gas production from natural gas. At present, the industrial production of synthesis gas from natural gas is based on high-pressure CH_4 reforming combined with CO shift. Among the advantages of these processes are reduced energy requirements in compressing the reformed gas whose volume is substantially greater than that of the feedstock, reduced size of the plant items, shorter interconnecting lines, fewer accessories, better recovery of waste heat from the wet gases (because the steam is condensed at a higher temperature), and simplified design of the $\text{H}_2 + \text{N}_2$ compressor. All of these factors provide a basis for the use of larger-capacity processing units and for the implementation of power cogeneration principle. The latter factor offers an added advantage in that the manufacturing cost of the product and the capital costs are cut down and the productivity is materially enhanced.

Wide use, both in and outside the Soviet Union, is made of a high-pressure process involving two steps of steam and steam-air reforming. It is the basis of tonnage plants embodying power cogeneration with a high degree of recovery of the heat of the catalytic reactions constituting the CH_4 reforming, CO shift, methanation, and ammonia synthesis operations.

The flowsheet of a 1360 t/d NH_3 synthesis plant effecting the two steps of CH_4 reforming and CO shift under high pressure is shown in Fig. 14.4.

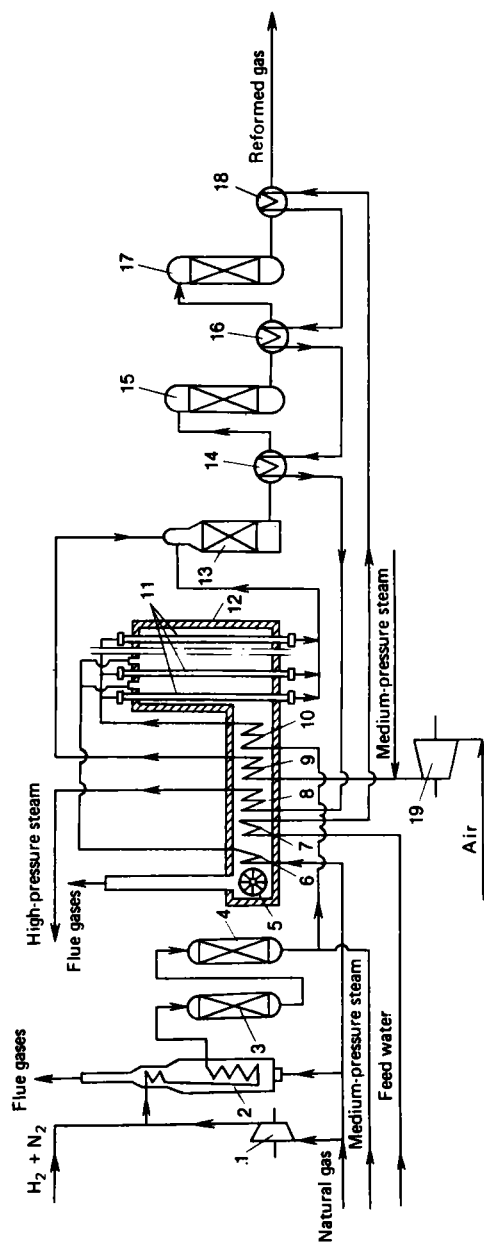


Fig. 14.4 Flowsheet of a two-stage gas reformer unit:

1, natural gas compressor; 2, direct-fired furnace-type heater; 3, desulphurizer; 4, adsorber; 5, smoke exhaust; 6, natural gas preheater; 7, feedwater preheater; 8, steam superheater; 9, steam-air preheater; 10, steam-gas preheater; 11, reaction tubes; 12, primary reformer; 13, secondary methane reformer; 14, steam boiler; 15, primary CO shift converter; 16, steam boiler; 17, secondary CO shift converter; 18, heat exchanger; 19, air compressor

Referring to the flowsheet, natural gas is compressed in a compressor 1 to a pressure of 4.6 MPa, mixed with an $H_2 + N_2$ mixture (in a 1:10 mixture to gas ratio), and fed into a direct-fired furnace-type heater, 2, where the feedstock is raised from 130-140 to 370-400 °C by burning natural or other combustible gas. Following that, the hot gas is desulphurized. For this purpose the organic sulphur compounds of the gas are hydrogenated over an Al-Co-Mo catalyst in a desulphurizer, 3, and the hydrogen sulphide thus obtained is then taken up by a zinc oxide-based sorbent in an adsorber, 4. As a rule, two adsorbers connected in series or in parallel are employed. One of them may be taken off stream so as to load a fresh charge of sorbent. The H_2S content of the scrubbed gas ought not to exceed 0.5 mg m^{-3} .

The scrubbed gas is mixed in a 1:3.7 ratio with steam, and the gas-steam mixture enters the convection zone of a primary tubular-type reformer. The radiation chamber of the primary reformer encloses tubes filled with a methane reforming catalyst, and burners which burn natural or any other fuel gas. The combustion gas thus produced heats the catalyst-filled tubes, and its heat is additionally reclaimed in the convection chamber which contains preheaters for the steam-gas and steam-air mixtures, a high-pressure steam superheater, and preheaters for high-pressure feed water and natural gas.

In preheater 10 the steam-gas mixture is raised to 525 °C and distributed in a downward flow among the large number of parallel-connected catalyst-filled tubes. The steam-gas mixture leaving the primary reformer carries 9-10 vol. % CH_4 . Heated to 850 °C, the reformed gas enters a secondary reformer, or combustor, 13, which is a shaft-type reactor. A compressor, 19, forces process air raised to 480-500 °C in the primary reformer's convection zone into the top portion of secondary reformer, 13. The steam-gas and steam-air mixtures enter the secondary reformer as separate streams and in a ratio required for a practically complete methane conversion to be achieved and for the reformed gas to be obtained with a $(CO + H_2):N_2$ ratio of from 1:3.05 to 1:3.10. The steam content answers a 0.7:1 steam-gas ratio. Maintained at around 1000 °C, the gas is routed to a waste heat boiler, 14, which raises steam at a pressure of 10.5 MPa. Here, the feedstock is cooled to 380-420 °C and enters the primary CO shift converter, 15, where the bulk of the CO reacts with steam over an iron-chromium catalyst. The gas mixture leaving the primary CO shift converter at 450 °C carries around 3.6 vol. % CO. In a steam boiler, 16, which likewise generates steam at a pressure of 10.5 MPa, the steam-gas mixture is cooled to 225 °C and fed to the secondary CO shift converter, 17, filled with a low-temperature catalyst. Here, the CO content is brought down to 0.5%. The reformed gas leaving converter 17 has the following composition (% by volume): H_2 , 61.7; CO, 0.5; CO_2 , 17.4; N_2 +

Ar, 20.1; and CH_4 , 0.3. After cooling and further waste heat recovery, the reformed gas at ambient temperature and a pressure of 2.6 MPa goes for scrubbing.

The two steps of the steam and steam-air high-pressure catalytic reforming of hydrocarbon gases and carbon monoxide shift constitute the first stage in a power cogeneration scheme of ammonia production. The heat of reaction from the conversion of CH_4 and CO, methanation and ammonia synthesis is reclaimed to heat high-pressure water and to raise superheated steam at a pressure of 10.5 MPa. This steam is used by the steam turbines that drive the compressors and pumps in the ammonia synthesis unit and is also utilized for process purposes.

The key item of the natural gas reforming unit is the tubular reaction furnace, or catalytic reformer. Several types of reformer exist, differing in pressure, type of tube sheets, shape of the combustion chamber, manner of heating, arrangement of convection chambers, feedstock, etc. The following types are most commonly used in industrial practice: multirow, terrace, two-tier, multi-tier with internal partitions, and with panel burners. Existing ammonia and methanol synthesis plants most often use straight-flow multi-row catalytic reformers flame-heated from above. A general view of the radiation chamber of a multirow catalytic reformer is shown in Fig. 14.5. The reformer consists of a radiation chamber and a convection chamber and is connected by a smoke flue to a smoke exhauster and a stack. The reformer is enclosed in a metal shell, 1. Its length is 26.1 m, the width of the radiation chamber is 21.5 m, and the structural depth of this

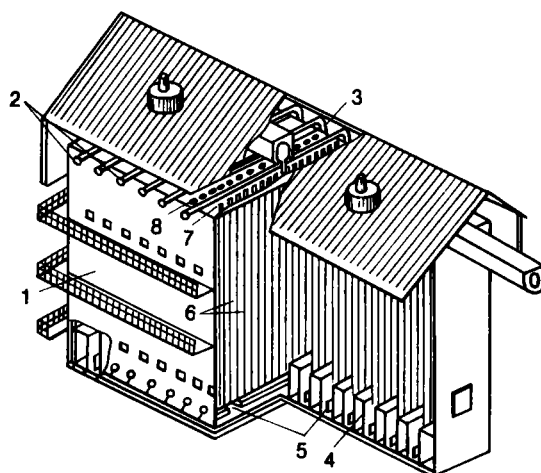


Fig. 14.5 Radiation chamber of a multirow catalytic reformer:

1, shell; 2, steam-gas headers; 3, reformed gas collector; 4, flues; 5, lower sectionalized headers; 6, reaction tubes; 7, gas-discharge tubes; 8, burners

chamber is 18.3 m. There is a start-up high-pressure boiler built as an adjunct to the convection chamber; it raises steam at a pressure of 10.5 MPa. As its name implies, the boiler serves to start up the plant and, if and when necessary, to supply some steam during the plant's operation. The radiation chamber encloses 12 vertical rows of tubes, 6 (a total of 504 tubes), each 71 mm ID, 21.5 mm wall thickness, and 10.75 m high.

The tubes are filled with a catalyst whose overall volume is 20.4 m³. The catalyst is in the form of rings of 15 mm OD, 7 mm ID, and 12 mm high. The maximum temperature of the tubes at a pressure of 3.7 MPa is 930 °C. The tubes are fabricated by centrifugal casting. Their material is an alloy containing 24-28% chromium and 18-22% nickel. The tubes are joined to the headers, 2, in such a way that they are free to expand when

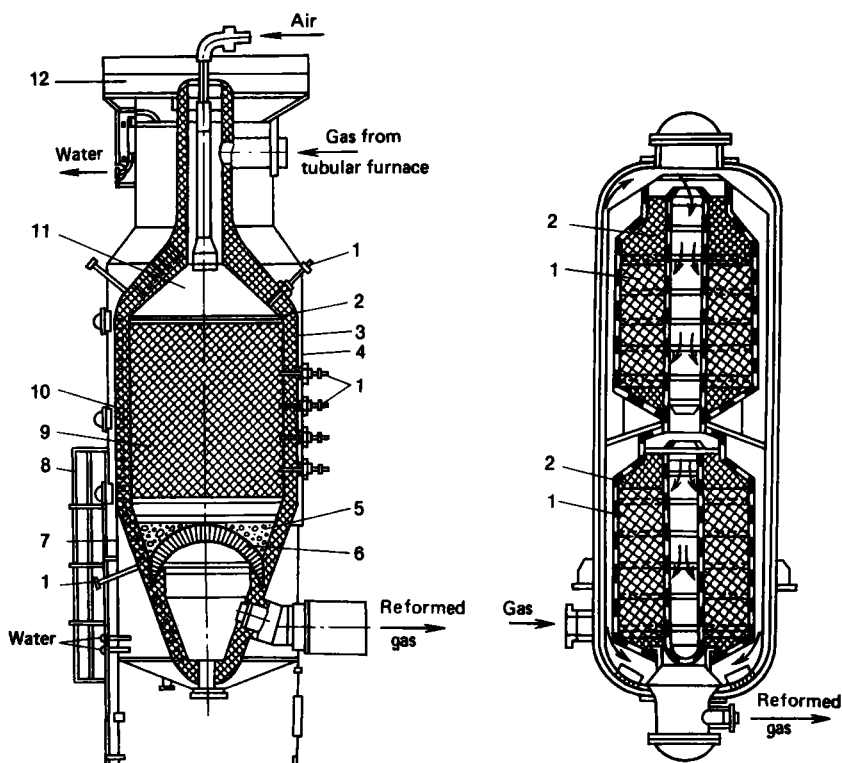


Fig. 14.6 Secondary methane reformer (combustor) of the shaft type:

1, thermocouples; 2, protective layer; 3, shell; 4, water jacket; 5, alumina balls; 6, arch; 7, support; 8, ladder; 9, catalyst; 10, lining; 11, mixing chamber; 12, upper service platform

Fig. 14.7 Radial-flow CO shift converter operating at a pressure of 2.0 MPa:

1, main catalyst beds; 2, stand-by catalyst beds

hot. Embedded in the roof of the radiation chamber and between the rows of reaction tubes are 260 injector-type flare burners, 8, to heat the tubes.

The U-shaped convection chamber encloses four preheaters and a high-pressure steam superheater which obtain their heat from the flue gases coming from the radiation chamber over the smoke flues, 4, at an inlet temperature of 1050 °C and leave the reaction furnace at an outlet temperature of 160-200 °C. The flue gases total 400 thousand $\text{m}^3 \text{hr}^{-1}$ in volume. More burners are installed in the flue upstream of the chamber and in the convection chamber. Their function is to supply an additional quantity of heat when necessary.

The secondary methane reformer, or catalytic combustor, (Fig. 14.6) is a vertical vessel with a mixing chamber, 11, at the top. Installed in the tapering bottom part of the vessel is an arch, 6, which gives support to alumina spheres, 5, in turn topped by a bed of nickel catalyst, 9, in the form of rings, totalling 38.5 m^3 in volume. The vessel is lined with high-temperature concrete, 10, and enclosed in a water jacket, 4, which will prevent dangerous temperature rises, should the liner fail. The vessel is 3.7 m ID and 17.4 m tall (including its foundation).

Figure 14.7 shows the arrangement of a radial CO shift converter. In this converter, the catalyst is held in a basket formed by the coaxially arranged central tube and outer shell whose surfaces on the process side are perforated and the perforations are covered by meshes on the catalyst side. The converter shell and the catalyst basket shell form an annular space through which the products are withdrawn or the feedstock is admitted.

As is seen, the flow pattern in the radial converter is a combination of an axial stream (through the annular space and the central tube) and a radial stream (through the catalyst bed).

14.3 Removal of Carbon Oxides from the Reformed Gas

Carbon oxides can be removed from the $\text{H}_2 + \text{N}_2$ mixture by absorption, adsorption, and catalytic processes.

Removal of carbon dioxide. Carbon dioxide can be removed from synthesis gas by various absorption processes. Originally, this was done by high-pressure water scrubbing. Unfortunately, the operation entailed the consumption of large quantities of electric power because of the low CO_2 solubility in water. As a rule, the water scrubbing step had to be supplemented by a further purification with, say, an alkaline solution.

Current practice is to remove the CO_2 with solutions of monoethanolamine (MEA) and potassium carbonate, K_2CO_3 . These chemisorbents have a high capacity and selectivity. Among their drawbacks is the consumption of large quantities of heat per cubic metre of

gas scrubbed when the original mixture has a high CO_2 concentration.

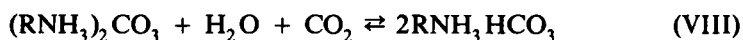
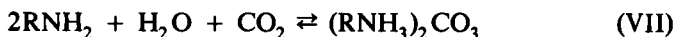
Because of this, some plants treat the reformed gas high in CO_2 with organic solvents, such as propylene carbonate (the Fluor process), N-methylpyrrolidone (the Purisol process), ethyl ether (the Selexol process), and refrigerated methanol (the Rectisol process).

In recent years, there has been a growing trend to effect the CO_2 removal with solutions of alkanolamines in organic solvents (so as to enhance the concentration of the active component in solution). Falling in this category are the Amisol process (based on a solution of diethanolamine and monoethanolamine in methanol) and the Sulphinol process (based on a solution of alkanolamine in sulpholane), to name but a few.

Except for the absorption by a NaOH solution, all of the above processes yield CO_2 as a by-product widely used in, say, urea manufacture.

In the Soviet Union, carbon dioxide is removed most often with a solution of monoethanolamine and a hot activated potassium carbonate solution.

CO_2 removal with monoethanolamine. This process is based on the fact that an aqueous solution of MEA reacts with CO_2 to form carbonates and bicarbonates which, when raised to a temperature of over 100°C , dissociate to evolve carbon dioxide. The process goes on according to the reactions



where $\text{R} = \text{OHCH}_2\text{CH}_2-$.

As follows from the above reaction schemes, 1 mole of amine combines with 1 mole of carbon dioxide. In practice, the carbonization of a saturated solution of MEA is 0.4-0.5 at atmospheric pressure and 0.6-0.75 at a pressure of 2.5-3.0 MPa.

As a rule, a 20% solution of MEA is used for CO_2 removal. It is not warranted to use solutions of a higher concentration for the following reasons: they would aggravate the corrosion of the equipment, more solvent would be lost, and the solution would be more viscous, thereby impairing the wettability of the packing and the coefficient of absorption.

Monoethanolamine solutions have a high absorbing capacity even at low partial pressures of CO_2 in the feed gas. Therefore, this process can be employed at atmospheric pressure.

As has been noted, when the temperature exceeds 100°C , reactions (VII) and (VIII) proceed to the left side with the evolution of carbon dioxide. This is the basis of the regeneration of spent MEA solutions. For

regeneration to take place, it is necessary to supply as much heat as follows from the heat balance for regeneration:

$$Q_r = Q_h + Q_{des} + Q_{ev} + Q_{loss}$$

where:

Q_r = heat of regeneration of the solution

Q_h = heat required to raise the solution to the regeneration temperature

Q_{des} = heat of desorption of the CO_2 driven off from solution

Q_{ev} = heat of vaporization (evaporation of water) when the CO_2 is driven off

Q_{loss} = heat lost to the surroundings

It is to be noted that most of the energy required for the MEA process is expended as heat to regenerate the absorbent. As a way of cutting down this expenditure and the cost of CO_2 removal in industrial-scale operation, measures are taken to reclaim as much heat of the hot regenerated solution, CO_2 and steam as possible. The heat lost to the surroundings is minimized by applying thermal insulation to the hot vessels and pipelines.

The key technical parameters of the MEA process are the pressure of absorption and regeneration, the temperature and concentration of the solution, and the degree of carbonization. Special care is taken when choosing these factors in ammonia manufacture because they have a vital bearing on the reliability and economy of the process.

The actual process scheme is to a great extent dependent on the overall plant setup. In the manufacture of ammonia and hydrogen based on the low-temperature CO shift conversion, the CO_2 is removed at a pressure of 1.0-3.0 MPa to a residual CO_2 content of 0.01-0.1%, followed by a further removal of CO and CO_2 by methanation.

In processes based on low-pressure steam-oxygen catalytic reforming followed by gas scrubbing with liquid nitrogen, it is necessary first to remove as much of the carbon dioxide present as practicable. For this purpose, resort is made to a two-step MEA process. At the first step, the reformed gas is treated at a pressure close to atmospheric so as to bring down the CO_2 content to 3-5 vol. %. During the second step effected at a pressure of 2.8 MPa, the CO_2 content is further reduced to a final value of 0.004 vol. %.

In the case of a high-pressure reforming process followed by scrubbing the reformed gas with liquid nitrogen, resort is likewise made to a two-step treatment, but the pressure is the same at both steps.

In existing 1360 t/d NH_3 synthesis units, the MEA process is modified to use separated streams of the absorbing solution. The flowsheet of this process is shown in Fig. 14.8.

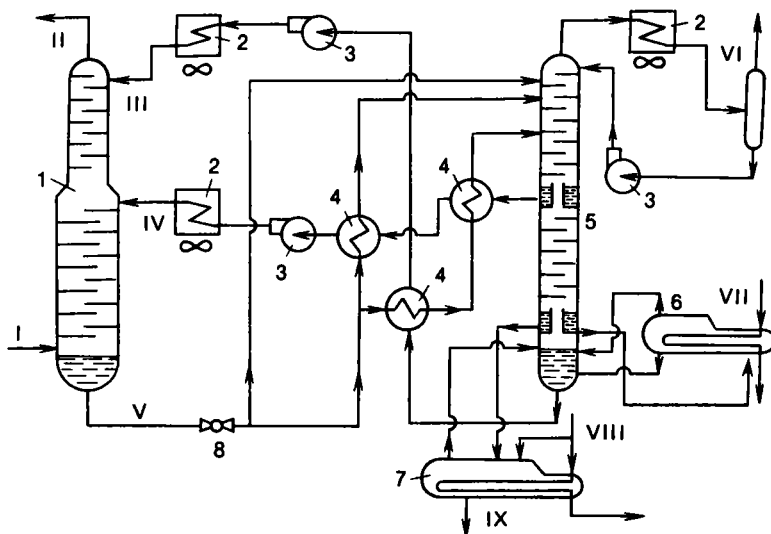


Fig. 14.8 Flowsheet for the monoethanolamine (MEA) process of CO_2 removal:

I, absorber; *2*, air cooler; *3*, pump; *4*, heat exchanger; *5*, regenerator; *6*, reboiler; *7*, pitch catcher; *8*, expansion valve; *I*, reformed gas; *II*, purified gas; *III*, highly regenerated liquor; *IV*, slightly regenerated liquor; *V*, saturated liquor; *VI*, carbon dioxide; *VII*, heat-transfer agent; *VIII*, steam; *IX*, still bottoms

Referring to the figure, the reformed gas at a pressure of 2.8 MPa and a temperature of 25–40 °C enters an absorber, *1*, equipped with sieve trays having a large bubble depth. The absorber consists of two sections. The lower section scrubs the gas to 5–7% CO_2 by volume, using a slightly regenerated solution. The upper section effects the fine scrubbing of the gas with a well-regenerated solution which, on taking up the CO_2 in the upper section to saturation, is mixed with the stream of the slightly regenerated solution and goes as a spray to the lower section. The carbonization of the saturated solution at the exit from the absorber is 0.65 mol CO_2 /mol amine. This solution is divided into three streams: one stream (around 10% of the total) goes to a tray at the top of the regenerator, *5* (the cold bypass); another stream (around 45% of the total) is raised to 90–95 °C in a heat exchanger, *4*, and fed to the middle portion of the regenerator; and the third stream equal to the second is further raised to 104–107 °C and enters the regenerator below the second stream (at the 18th tray). At the top of the regenerator, the solution is subjected to primary regeneration so that the CO_2 content is 0.3–0.35 mole per mole of amine. Then the solution is subdivided into two approximately equal streams: one enters heat exchanger *4* on the tube side, is cooled to 70 °C, forced by a pump, *3*, through an air cooler, *2*, and enters at a temperature of 40 °C as a spray the lower section of the absorber. The other stream

moves through downflow tubes inside the regenerator and enters the lower section where the solution is subjected to further (fine) regeneration.

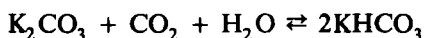
The final desorption of CO_2 from the solution takes place in a reboiler, 6, usually heated by the reformed gas. The highly regenerated solution is cooled to 70 °C in heat exchanger 4 and transferred by pump 3 to air cooler 2 where it is cooled to 40 °C. The cooled solution is returned to irrigate the upper section of the absorber.

The steam-gas mixture leaves the regenerator at a temperature of 75-85 °C and a pressure of 0.17 MPa, is cooled in the air cooler where the steam condenses, and the condensate is separated in a separator from which the cooled CO_2 is withdrawn.

Anywhere between 0.5 and 1% (by weight) of the circulating solution is continuously withdrawn from the lower section of the regenerator. It is routed to a resin catcher, 7. Here, the temperature is gradually raised to 145 °C in the presence of live steam, and the MEA is distilled off from the high-molecular-weight resins that are formed during the operation. The MEA vapour and steam are routed from the resin catcher to the regenerator reboiler.

The distillation of the MEA solution, which is provided for in all existing plants, is a major factor in reducing the amine loss, preventing foam formation, and minimizing corrosion. Importantly, the MEA process provides for a high degree of CO_2 removal and permits the use of small-size plant items.

CO_2 removal by a hot activated potassium carbonate solution. The basis of this process is the reversible reaction



The process is effected at elevated temperature as this enhances the solubility of the potassium carbonate in water and the rate of chemisorption.

It has been found that the rate at which a hot potassium carbonate solution absorbs CO_2 markedly increases when the solution is activated with some additives. At one time, it was customary to add compounds of trivalent arsenic, but this practice has now been abandoned because of arsenic toxicity. At present, it is widely practised to add diethanolamine (DEA) to the hot potassium carbonate solution. The best results are usually obtained with an aqueous solution containing 28 wt % K_2CO_3 and 1.5-2 wt % DEA. In order to minimize corrosion, a fraction of one percent of vanadium oxide is also added to the solution.

The flowsheet of the DEA process is shown in Fig. 14.9. This is a simplified version of the two-stream scheme used in 1360 t/d NH_3 synthesis units.

The desorption of CO_2 from the solution takes place in a hydraulic turbine, 9, as the pressure is reduced from 2.8 to 0.65 MPa and due to the subsequent boiling. About 80% of the slightly regenerated liquor is withdrawn from the upper section of the regenerator and routed to the lower section of the absorber. The remaining 20% of the solution is regenerated in the lower section of the regenerator and in a reboiler, 5. The pressure in the regenerator reboiler is 0.17 MPa. Highly regenerated liquor *III* is cooled in a heat exchanger, 7, and an air cooler, 3, and routed to the upper section of the absorber. Around 2% of the total solution stream is continuously filtered by activated carbon in a filter, 6.

The mixture of CO_2 and steam leaving the regenerator at around 102°C is cooled, separated in separator 2 from solvent droplets and is either utilized in the process or discharged to the atmosphere.

Removal of carbon monoxide. After CO_2 removal, the reformed gas is treated for CO removal. Originally, it was widely practised to remove the carbon monoxide with a copper-ammonium carbonate solution. Unfortunately, this process goes on at a low rate and poses problems with regard to temperature control. At existing plants, the gas is preferably scrubbed with liquid nitrogen. In this process, the liquid nitrogen dissolves both the carbon monoxide and methane and argon so that the resultant $\text{H}_2 + \text{N}_2$ mixture is thoroughly cleaned of catalyst poisons and inert substances. The CO content of the mixture is not over $20\text{ cm}^3\text{ m}^{-3}$.

A simplified flowsheet for the liquid nitrogen scrubbing of the reformed gas is shown in Fig. 14.10. The reformed gas is cooled in a pre-ammonia heat exchanger by a stream of nitrogen-activated mixture, and the moisture thus condensed is separated in a separator, 2. The gas is further cooled in an ammonia cooler, 3, due to the evaporation of ammonia outside the

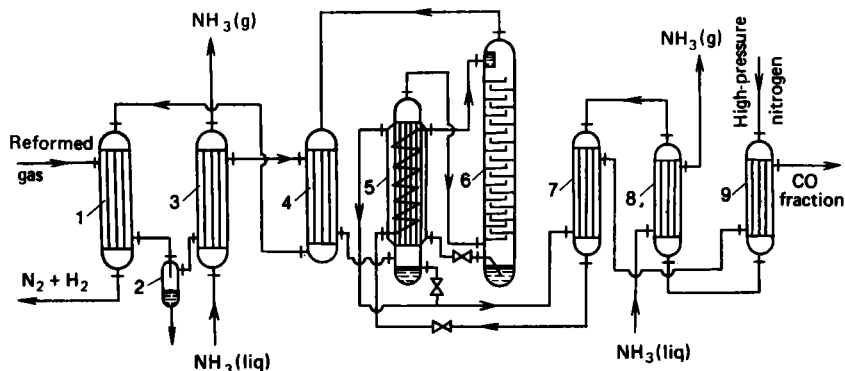


Fig. 14.10 Flowsheet for the scrubbing of synthesis gas with liquid nitrogen:

1, heat exchanger; 2, separator; 3, ammonia cooler; 4, heat exchanger; 5, vaporizer; 6, scrubbing column; 7, heat exchanger; 8, ammonia cooler; 9, heat exchanger

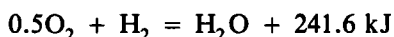
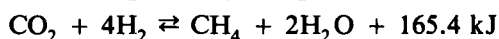
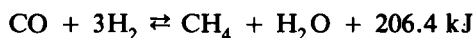
tubes, and finally cooled to -186°C by a stream of cold $\text{H}_2 + \text{N}_2$ mixture in a heat exchanger, 4. Following that, the gas is allowed to pass through a vaporizer, 5, where it is cooled to -192°C by the CO fraction. As a result, the carbon monoxide, methane and argon are condensed from the gas which then enters a multiple-tray scrubber, 6, countercurrent to the pure liquid nitrogen entering the scrubber from above. In this way, the gas finally gets rid of its CO, CH_4 and Ar which dissolve in the liquid nitrogen.

On leaving the scrubber at -190 to -193°C , the gas enters heat exchangers 4 and 1 to cool the reformed gas and goes, raised to $20-30^{\circ}\text{C}$, to ammonia synthesis.

Pure gaseous nitrogen compressed to 19.6 MPa is cooled by the CO fraction in a heat exchanger, 9, and also to -45°C in an ammonia cooler, 8. On passing through a moisture catcher, drier and filter (not shown in the flowsheet), the high-pressure nitrogen is cooled to -184°C by the CO fraction in a heat exchanger, 7, expanded to a pressure of 2.6 MPa and is further cooled in the meantime, passes through the coil of vaporizer 5, is fully liquefied, and enters scrubber 6 as reflux.

The liquid CO fraction leaving the lower section of scrubber 6 is expanded to a pressure of 0.05 MPa and joins the main body of the CO stream leaving vaporizer 5. The cold of this fraction is then reclaimed in heat exchangers 7 and 9.

Methanation. Final removal of CO and CO_2 from the $\text{H}_2 + \text{N}_2$ mixture in existing ammonia synthesis units is effected via the catalytic hydrogenation of these compounds to methane in a methanator according to the reactions:



The hydrogenation is effected over a catalyst at $250-350^{\circ}\text{C}$. In these conditions, the reactions are practically irreversible and proceed to completion with the evolution of much heat. The methanation catalyst is a pre-reduced nickel-aluminium catalyst available as pellets measuring from 4-5 to 8-10 mm across.

A flowsheet for catalytic hydrogenation (methanation) is shown in Fig. 14.11. The synthesis gas supplied at a pressure of 2.7-2.8 MPa is raised to 300°C by a steam-gas mixture in heat exchangers, 1 and 2, and admitted to a methanation reactor, 3, from above. The methanator is a vertical cylindrical vessel 3.8 m in diameter and 7.6 m tall. It can hold as much as 40 m^3 of catalyst. The scrubbed $\text{H}_2 + \text{N}_2$ mixture is raised by the heat of hydrogenation to 350°C , and gives up its heat on consecutively passing through a high-pressure water preheater, 4, a low-pressure water preheater,

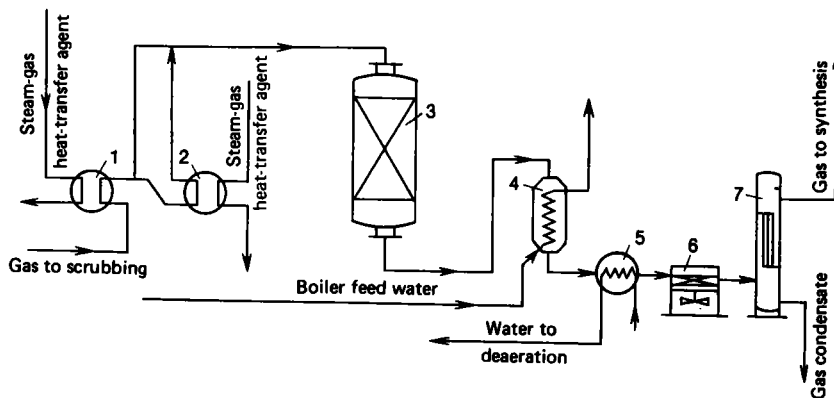


Fig. 14.11 Flowsheet of a catalytic hydrogenation unit:

1, gas heat exchanger; 2, gas heat exchanger; 3, methanator; 4, water preheater; 5, water preheater; 6, air cooler; 7, moisture separator

5, and an air cooler, 6. Following that, the gas mixture is routed to a water separator, 7, where it gets rid of the water condensed by cooling. Maintained at a temperature of 35 °C, the $H_2 + N_2$ mixture enters a high-pressure compressor from which it goes to ammonia synthesis.

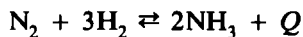
The methanation process is simple, easy to control, and readily fits into power cogeneration schemes of ammonia synthesis.

14.4 Ammonia Synthesis

Ammonia is the key component of many nitrogen-bearing compounds used in industry and agriculture. D.N. Pryanishnikov of Russia has called ammonia “the alpha and omega” of nitrogen metabolism in plant life.

The composition of ammonia was determined by C. Berthollet in 1784. Ammonia, NH_3 , is a base, a moderately strong reducer, and an efficient complexing agent with respect to cations possessing vacant bond orbitals.

Physico-chemical principles of the process. Ammonia synthesis from the elements nitrogen and hydrogen is effected according to the scheme



This is a reversible, exothermic reaction — it has a large negative change of enthalpy on reaction ($\Delta H_{298} = -91.96 \text{ kJ mol}^{-1}$) and becomes still more exothermic at elevated temperatures ($\Delta H_{725} = -112.86 \text{ kJ mol}^{-1}$). By Le Chatelier’s principle, heating shifts the equilibrium position to the left, that is, towards a lower yield of ammonia. The entropy change is likewise negative ($\Delta S_{298} = -198.13 \text{ kJ mol}^{-1} \text{ K}^{-1}$) and does not favour the progress of the reaction. When ΔS is negative, a rise in temperature makes the reaction less probable because ΔS governs the dependence of ΔG on

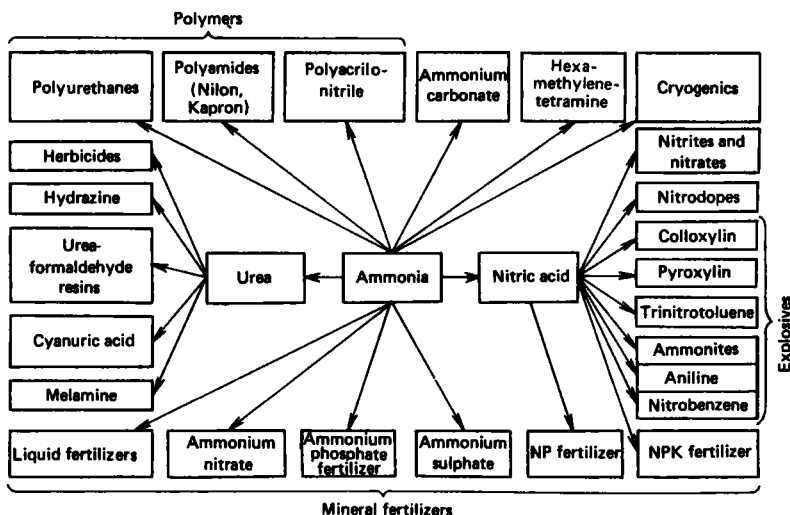


Fig. 14.12 Applications of ammonia

temperature according to the equation

$$(\partial \Delta G / \partial T)_p = -\Delta S = (\Delta G - \Delta H) / T \quad (14.1)$$

The ammonia synthesis reaction proceeds with a decrease in the number of moles. As follows from the reaction equation, 4 moles of the synthesis gas form 2 moles of gaseous product. Proceeding from Le Chatelier's principle, it may be concluded that at equilibrium the ammonia content of the mixture will be greater at a higher than at a lower pressure.

The extent of chemical change can be predicted from the equilibrium constant. For the synthesis reaction the equilibrium constant

$$K_p = p_{\text{NH}_3, e} / p_{\text{N}_2, e}^{1/2} p_{\text{H}_2, e}^{3/2}$$

is found by experiment.

The manner in which the equilibrium constant depends on temperature and pressure is illustrated in Table 14.2.

If we know the equilibrium constants, we can find the equilibrium concentrations of ammonia at any temperature and pressure. On denoting the mole fraction of ammonia in equilibrium mixture as x_e and subject to the reaction equation, we get at equilibrium $(1 - x_e)$ moles of N_2 , $(3 - 3x_e)$ moles of H_2 and $2x_e$ moles of NH_3 . The total number of moles is

$$1 - x_e - 3 - 3x_e + 2x_e = 4 - 2x_e$$

The partial pressures of the mixture components are as follows.

$$p_{\text{N}_2} = [(1 - x_e) / (4 - 2x_e)] p$$

Table 14.2 Equilibrium Constant for Ammonia Synthesis as a Function of Temperature and Pressure

Temperature, °C	Equilibrium constant					
	1	5	Pressure, MPa:		60	100
			10	30		
200	.64880	.69780	.73680	.91200	2.49300	10.35000
300	.06238	.06654	.06966	.08667	0.17330	0.51340
400	.01282	.01310	.01379	.01717	.02761	.06035
500	.00378	.00384	.00409	.00501	.00646	.00978
600	.00152	.00146	.00153	.00190	.00200	.00206
700	.00071	.00066	.00070	.00087	.00085	.00052

$$p_{\text{H}_2} = [(3 - 3x_e)/(4 - 2x_e)]p$$

$$p_{\text{NH}_3} = [2x_e/(4 - 2x_e)]p$$

where p is the total pressure of the mixture at equilibrium. On substituting the partial pressures into Eq. (14.2), we obtain

$$K_p = \frac{2x_e p \times 2^{1/2}(2 - x_e)^{1/2} \times 2^{3/2}(2 - x_e)^{3/2}}{2(2 - x_e)(1 - x_e)^{1/2} p^{1/2} \times 3^{3/2}(1 - x_e)^{3/2} p^{3/2}}$$

$$= [4(2 - x_e)x_e]/[3^{3/2}(1 - x_e)^2 p] \quad (14.3)$$

On solving Eq. (14.3) for x_e , we obtain a design equation by which to find the equilibrium concentration of ammonia at any temperature and pressure:

$$x_e = 1 + 1.54/K_p p - [(1 + 1.54/K_p p)^2 - 1]^{1/2} \quad (14.4)$$

Thus, from a qualitative and quantitative evaluation of conditions for thermodynamic equilibrium we may conclude that a maximum ammonia yield can be obtained by effecting the process at a high pressure and a low temperature. However, the synthesis process in a homogeneous gas phase is practically unfeasible even at very high temperatures (in excess of 1000 °C).

Ammonia synthesis proceeds at a noticeably high rate only in the presence of a solid catalyst. The heterogeneous catalytic synthesis of ammonia occurs by a complex mechanism which may be visualized as consisting of the following steps:

(1) Nitrogen and hydrogen molecules diffuse to the surface of the catalyst.

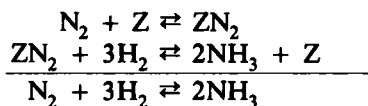
(2) The reactant molecules (adsorbates) are chemisorbed on the surface of the catalyst.

(3) A surface chemical reaction takes place with the formation of intermediate complexes and the complexes react with one another.

(4) The product is desorbed.

(5) The product (ammonia) diffuses from the catalyst surface into the gas phase.

Studies into the kinetics and mechanism of ammonia synthesis have shown that the rate-controlling step here is the chemisorption of nitrogen. In the light of this finding, the mechanism of ammonia synthesis may be summarized as follows:



where Z is a free site on the catalyst surface and ZN_2 is a chemisorbed species (adsorbate).

The rate of the reversible ammonia synthesis reaction from the elements hydrogen and nitrogen, effected over most of the known catalysts, may be described by the Temkin-Pyzhev equation:

$$dp_{\text{NH}_3}/d\tau = k_1 p_{\text{N}_2} (p_{\text{H}_2}^3 / p_{\text{NH}_3}^2)^\alpha - k_2 (p_{\text{NH}_3}^2 / p_{\text{H}_2}^3)^{1-\alpha} \quad (14.5)$$

where:

- k_1 = rate constant of ammonia formation
- k_2 = rate constant of ammonia decomposition
- p_{N_2} = partial pressure of nitrogen
- p_{H_2} = partial pressure of hydrogen
- p_{NH_3} = partial pressure of ammonia
- α = constant such that $0 < \alpha < 1$, which gives the fraction of the catalyst's surface covered by nitrogen. For iron catalysts, α is 0.5 in the temperature range 400-500 °C.

The rate of the ammonia synthesis reaction depends on temperature, pressure and feedstock composition. Their values are taken as optimal if the process rate is a maximum. The optimum synthesis temperature, T_m , can be determined by differentiating Eq. (14.5) with respect to temperature, and equating the derivative to zero. The resulting expression has the form

$$T_m = \frac{\Delta H}{R \ln (k_{20} E_2 p_{\text{NH}_3}^2 / k_{10} E_1 p_{\text{N}_2} p_{\text{H}_2}^3)} \quad (14.6)$$

It follows from Eq. (14.6) that the optimum temperature falls with an increase in the ammonia content of the recycled gas and a decrease in the $\text{H}_2 + \text{N}_2$ mixture content.

It is also seen from the Temkin-Pyzhev equation that the rate of the forward synthesis reaction is proportional to $p^{1.5}$ and that of the backward reaction is inversely proportional to $p^{0.5}$. It follows then that a rise in pressure entails an increase in the observed rate of the process.

From thermodynamic and kinetic considerations, the ammonia synthesis process should preferably be effected at elevated pressure (there is an increase in equilibrium yield and synthesis rate). High pressure also favours ammonia condensation. On the other hand, an increase in pressure calls for the use of more electric power to drive compressors and makes more stringent the requirements to be met by the plant. At lower pressure, simpler reaction vessels may be used and less energy is required, but the plant items have to be made bigger in size, more power has to be expended to recirculate the gas and to separate the ammonia, and the synthesis gas must be of higher purity.

The optimum pressure for ammonia synthesis has been found on the basis of a complex mathematical model of the plant. The objective function in this model is the discounted costs:

$$C_d = C_m + EC_c / T \quad (14.7)$$

where:

C_d = discounted costs, roubles / t

C_m = manufacturing cost of ammonia, roubles / t

C_c = capital costs, roubles

E = standard efficiency factor, yr^{-1}

T = plant throughput, t / yr ammonia

The computational results are presented in the plot of Fig. 14.13. As is seen, the discounted and capital costs tend to decrease with increasing pressure. An analysis has shown that the pressure of choice for existing production schemes is around 30 MPa.

Since the presence of inert impurities in the feedstock is equivalent to a decrease in the total pressure, an increase in the methane, argon and helium content of the feed mixture causes the reaction rate to fall.

From an analysis of Eq. (14.5) it is seen that the rate of the forward reaction is inversely proportional and that of the backward reaction is directly proportional to the partial pressure of the ammonia. Thus, an increase in the ammonia content leads to a fall in the reaction rate. An increase in the volumetric flow rate of the feedstock cuts down the increase in the ammonia content, thereby causing the mean rate and the process throughput to rise.

The ammonia content of the $\text{H}_2 + \text{N}_2$ mixture of a stoichiometric composition as a function of temperature, pressure and volumetric flow rate for an industrial catalyst is shown in the plots of Fig. 14.14a, b and c.

C_d , roubles/tonne NH_3

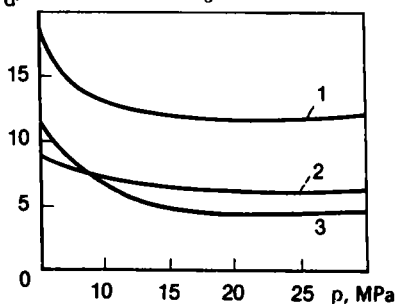


Fig. 14.13 Dependence of (1) discounted, (2) capital and (3) specific utility costs on pressure at the compression, ammonia synthesis and condensation steps

The ammonia synthesis reaction is a reversible one. Therefore, a single pass of the feedstock through the reactor fails to lead to a complete conversion of hydrogen and nitrogen. The equilibrium conditions and kinetics of the process over iron catalysts are such that a mere 20 to 40% of the original feed can be converted to ammonia. If a higher conversion is to be assured, the feedstock must be passed through the reactor more than once. All existing ammonia synthesis units operate with a recycle — the product ammonia is withdrawn and the unreacted $\text{H}_2 + \text{N}_2$ mixture goes back to the synthesis step.

The product ammonia is separated by cooling it along with the $\text{H}_2 + \text{N}_2$ mixture to the liquefaction point of ammonia. Complete condensation of ammonia cannot be obtained, and some of it is left in the $\text{H}_2 + \text{N}_2$ mixture. The ammonia concentration in an $\text{H}_2 + \text{N}_2$ mixture containing inert gases, as measured at saturation, at a pressure of 30 MPa and several values of temperature is given below.

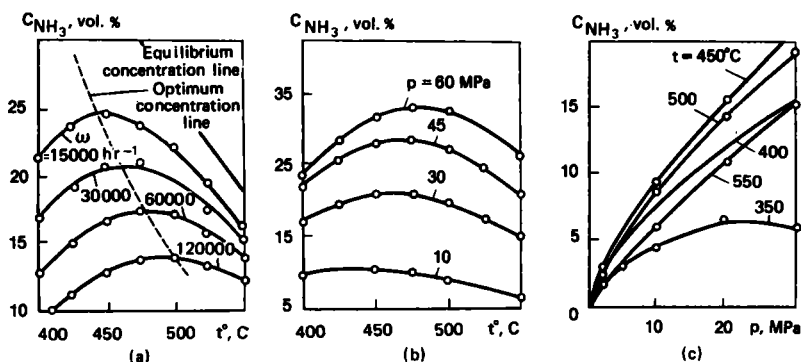


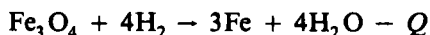
Fig. 14.14 Ammonia content as a function of: temperature: (a) at various volumetric flow rates ($p = 30$ MPa); (b) at various pressures (volumetric flow rate, 30,000 hr^{-1}); (c) pressure at various temperatures (volumetric flow rate, 30,000 hr^{-1})

$T, ^\circ\text{C}$	-20	-10	0	5	10	15	20	25
$C_{\text{NH}_3}, \text{vol. } \%$	1.5	2.15	3.2	4.0	4.75	5.5	6.2	7.3

It follows from the above data that when the pressure is 30 MPa the gas must be cooled to a temperature in the range from -5° to 0°C . To achieve this, the mixture is cooled, in addition to water or air coolers, by boiling liquid ammonia. In plants operating at a higher pressure (say, 60 to 100 MPa), the ammonia can be separated from the $\text{H}_2 + \text{N}_2$ mixture by cooling it solely with air or water. The unreacted feedstock and the residual ammonia are recycled to the ammonia synthesis step.

Ammonia synthesis catalysts. High catalytic activity in ammonia synthesis is displayed by Group VI, VII and VIII metals. Those most active are Fe, Ru, Re, and Os. Commercial plants mostly use iron catalysts produced by fusing iron oxides with promoters and then by reducing the iron oxides. The promoters may be acidic and amphoteric oxides, such as Al_2O_3 , SiO_2 and TiO_2 , and also the oxides of alkali and alkali-earth metals, such as K_2O , Na_2O , CaO , and MgO .

The reduction of a catalyst may be described by the following overall reaction equation



Ammonia synthesis catalysts are permanently poisoned by sulphur compounds and chlorine. The overall poison content of the feedstock may not exceed 0.5 ppm.

When present in the feedstock, oxygenated compounds (H_2O , CO and CO_2) and oxygen act as strong catalyst poisons, but they affect the activity of a catalyst temporarily, that is, reversibly. Their poisoning effect is directly proportional to the oxygen content. If the fresh feed gas carries oxygenated impurities or oil, it should be put into the process ahead of the second condensation step so as to remove the objectionable compounds with the condensed ammonia.

Ammonia synthesis equipment. Ammonia synthesis units may be classified according to their operating pressure into low-pressure (10.0-16.0 MPa), medium-pressure (20.0-50.0 MPa), and high-pressure (80.0-100.0 MPa). Originally, low-pressure units operated at a pressure of 10.0 MPa and a low temperature (400°C). Their yield was 8-13 vol. % ammonia owing to the use of an active catalyst which consisted of a complex salt containing iron cyanide. At present, low-pressure ammonia synthesis units evoke interest for the reason that they need less energy for the compression and recirculation of the process gas — a major utility item in ammonia manufacture. In several newer production schemes, ammonia synthesis will be effected at the same pressure as the production of synthesis gas (below 10 MPa).

High-pressure ammonia synthesis units were a common occurrence in the 1930s and 40s. The process was effected at a pressure of 90-100 MPa — a factor conducive to a high conversion (40%) of the $H_2 + N_2$ mixture. Such units are no longer built.

At this writing, preference in the nitrogen industry the world over is given to medium-pressure units. Those operating in the Soviet Union use a pressure of 30-36 MPa. There are several units which operate at a pressure of 45 MPa. The plants under construction are mainly designed for a pressure of 32 MPa.

In present-day ammonia synthesis plants of large unit capacity, the process is effected over fused iron catalysts at a temperature of 420-500 °C, a pressure of 25-32 MPa, and a volumetric flow rate of 15-25 thousand $m^3\ hr^{-1}$. The output is 20-40 t/d of ammonia per cubic metre of catalyst.

Figure 14.15 shows a flowsheet for ammonia synthesis on a Soviet-built 1360 t/d plant.

Referring to the flowsheet, the fresh $H_2 + N_2$ mixture after it has been purified by methanation is compressed in a centrifugal compressor to a pressure of 32 MPa. Following that, it is cooled in an air cooler (not shown in the diagram) and enters the lower section of a condensation tower, 8, for removal of the residual CO_2 and H_2O and traces of oil. In the tower, the gas is bubbled through a layer of condensed liquid ammonia, gets rid of its water vapour, CO_2 and oil, is saturated with ammonia to 3-5%, and mixed with the recycled gas. The resultant mixture is passed through the tubes of the heat exchanger in the condensation tower and enters the intertubular space of an external heat exchanger, 4, where it is heated to 185-195 °C by the hot gas leaving the ammonia reactor or converter. Following that, the recycled gas enters the ammonia synthesis reactor, 2.

In the reactor, the gas moves upwards through the annular clearance between the tower shell and the packing shell and enters the shell side of the internal heat exchanger located in the neck of the ammonia synthesis reactor. In the heat exchanger, the recirculated gas is heated to the kindling temperature of the reaction (400-440 °C) by the hot reformed gas and passed consecutively through the four catalyst beds so that the ammonia content of the gas is raised to 15%. Heated to 500-515 °C, the $H_2 + N_2 + NH_3$ mixture passes through the central pipe and enters the internal heat exchanger where it is cooled to 330 °C. The gas mixture is further cooled to 215 °C in the tubes of feedwater preheater 3, to 65 °C in the tubes of external heat exchanger 4 by the cold recirculated gas which moves on the shell side, and finally to 40 °C in air coolers 7, with a sizeable proportion of the ammonia being condensed. The condensed ammonia is then separated in a separator, 6, and the mixture carrying 10-12% NH_3 goes to the circulating impeller of an $H_2 + N_2$ compressor, 5, where it is compressed to a pressure of 32 MPa.

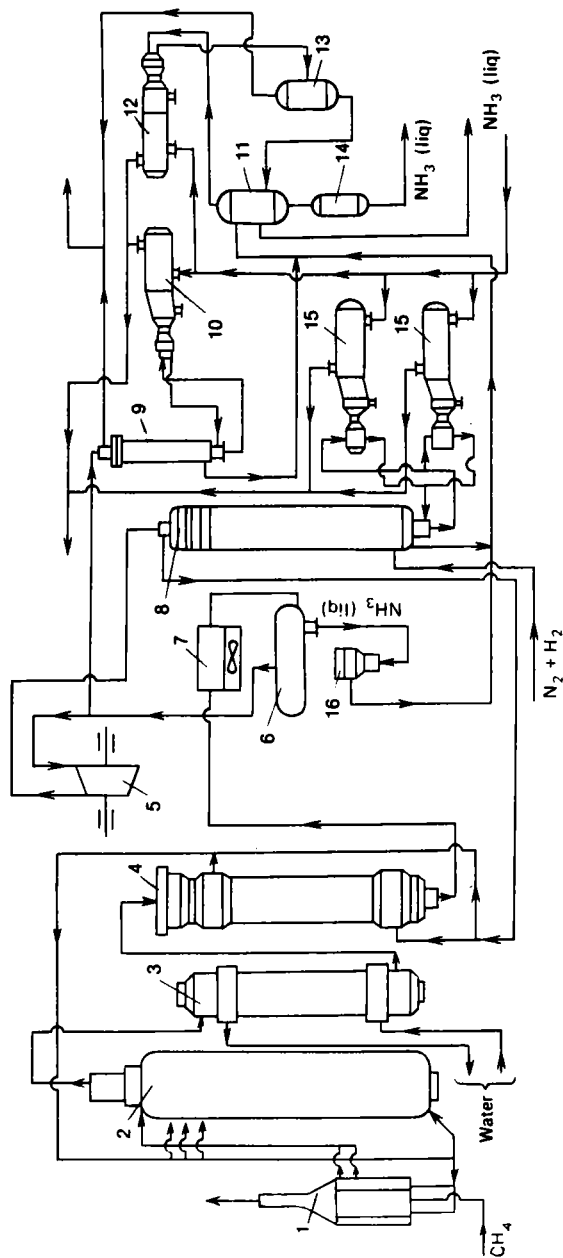


Fig. 14.15 Process flowsheet of a 1360 t/d ammonia synthesis unit:

1, preheater; 2, ammonia synthesis reactor; 3, water preheater; 4, external heat exchanger; 5, compressor impeller; 6, liquid ammonia separator; 7, air cooler bank; 8, condensation tower; 9, purge-gas condensation tower; 10, liquid ammonia vaporizer; 11, liquid ammonia collector; 12, liquid ammonia vaporizer; 13, liquid ammonia venting tank; 14, intermediate venting tank; 15, liquid ammonia venting tank; 16, magnetic filter

Maintained at a temperature of 50 °C, the recirculating gas enters the secondary condensation step which includes the condensation tower, 8, and liquid ammonia vaporizers, 15. The gas is cooled to 18 °C in the condensation tower and to -5 °C in the vaporizers as the ammonia boils on the shell side. A mixture of the cooled circulating gas and condensed ammonia leaves the tube side of the vaporizer and enters the separation section of the condensation tower where the liquid ammonia is separated from the gas and the fresh $H_2 + N_2$ mixture is mixed with the circulating gas. Following that, the gas mixture passes through a basket holding porcelain Raschig rings, where it gets rid of the entrained droplets of liquid ammonia, flows up the tubes of the heat exchanger, and is routed first to external heat exchanger 4, then to reactor 2.

The liquid ammonia collected in the primary separator is passed through a magnetic filter, 16, for removal of catalyst dust and mixed with the liquid ammonia from condensation tower 8. Following that, it is expanded to a pressure of 4 MPa and routed to a liquid ammonia collector, 11. As the liquid ammonia is expanded to a pressure of 4 MPa, it gives up its dissolved gases H_2 , N_2 , O_2 , and CH_4 . These 'tank' gases, as they are called, carry 16-18% NH_3 . Therefore they are transferred to a vaporizer, 12, so as to reclaim the ammonia by condensing it at -25 °C. On leaving the vaporizer, the tank gases and the condensed ammonia go to a separator, 13, for removal of liquid ammonia which is then routed to liquid ammonia collector 11.

Following the primary ammonia condensation step (downstream from separator 6), the gas is purged so as to hold the inert gas content of the recycled gas at not over 10%. The purge gas carries 8-9% NH_3 which is separated at a temperature of -25 to -30 °C in condensation tower 9 and liquid ammonia vaporizer 10. Upon separation of the ammonia, the mixture of tank and purge gases is used as a fuel gas.

Plant items. *The ammonia synthesis reactor.* Most commonly 1360 t/d NH_3 synthesis units use axial four-stage packed ammonia synthesis reactors with an upflow heat-exchanger or three-stage converters with an external heat exchanger.

Figure 14.16 shows in sketch form an axially packed four-stage ammonia converter. The main body of the gas stream enters the converter at the bottom, moves through the annular clearance between the converter shell, 15, and the catalyst box shell, 3, and fills the shell side of heat exchanger 6. Here, the synthesis gas is heated by the reformed gas to 420-440 °C and passes through the four catalyst beds, 8, 10, 12, and 14, between which a cold bypass gas is admitted. On passing through the fourth catalyst bed, the gas mixture at 500-515 °C flows up the central pipe, 2, passes through the tubes of heat exchanger 6, is cooled to 320-350 °C in the process, and leaves the reactor.

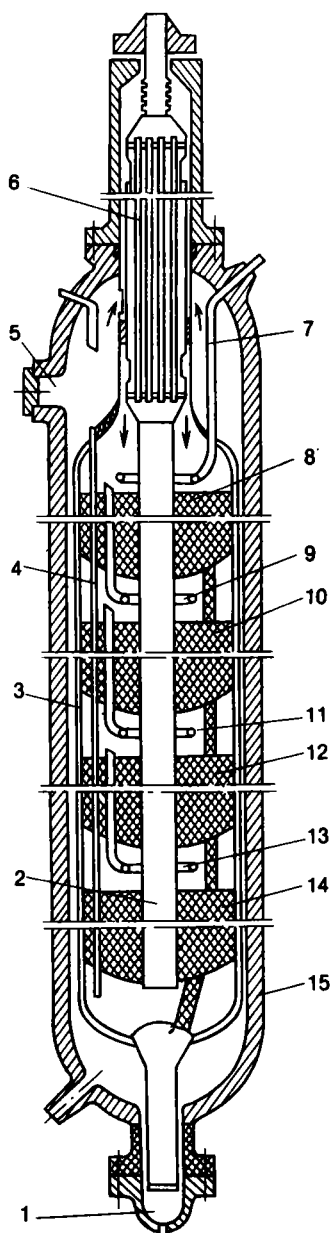


Fig. 14.16 Four-stage ammonia synthesis reactor of a 1360 t/d unit:

1, catalyst discharge port; 2, central pipe; 3, catalyst box shell; 4, thermocouple jacket; 5, charging port; 6, heat exchanger; 7, bypass gas inlet; 8, catalyst bed; 9, bypass gas inlet; 10, catalyst bed; 11, bypass gas inlet; 12, catalyst bed; 13, bypass gas inlet; 14, catalyst bed; 15, reactor shell

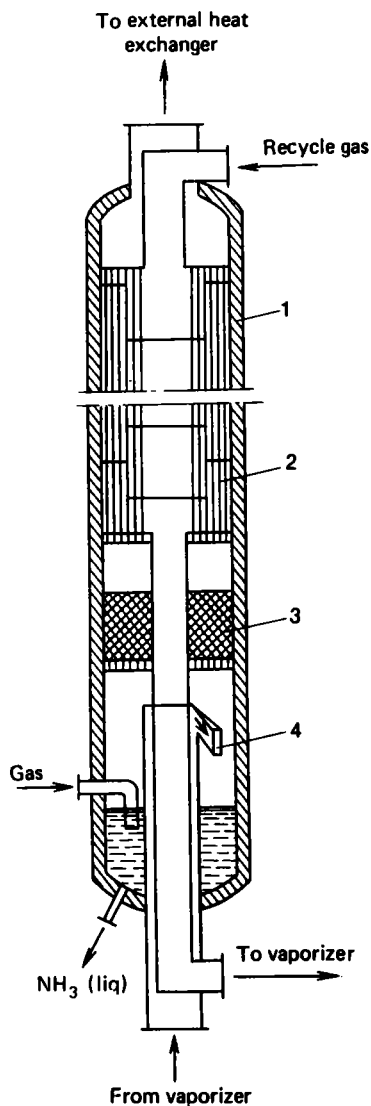


Fig. 14.17 Condensation tower:

1, shell; 2, heat exchanger; 3, spray catcher; 4, separator

The technical particulars of the ammonia synthesis reactor are as follows.

Pressure	31.5 MPa
Operating temperature	300-520 °C
Inside diameter	2.4 m
Height	32 m
Wall thickness	250 mm
Catalyst volume per stage (from I through IV)	7, 8.4, 12.8, and 14.7 m ³

The condensation tower. This is a vertical cylindrical vessel 2 m ID and 18.89 m tall (Fig. 14.17). It consists of a heat exchanger and a separator located below the heat exchanger which has a total of 7808 tubes each 14 mm OD, 2 mm ID and 7.21 m high. The heat exchange surface area (as measured over the mean diameter) is 2120 m². The shell side encloses baffles. The gas being cooled flows on the shell side, and the gas remaining after ammonia separation on the tube side.

The gas cooled in the vaporizer is admitted via the lower connection into a separation fixture, 4, where the gas stream is whirled so that the liquid detaches itself from the gas stream, collects at the bottom of the vessel and is continuously withdrawn. The gas moves upwards, passes through a spray catcher, 3, consisting of a bed of Raschig rings, and flows through the tubes, giving up its cold in the process. The fresh gas entering by a side connection in the bottom of the vessel bubbles through the liquid ammonia layer and gets rid of its water vapour and carbon dioxide.

Environmental pollution abatement in ammonia manufacture. A tonnage ammonia synthesis plant will usually be responsible for the following emissions and effluents:

- (1) Gas emissions carrying ammonia, nitrogen oxides, carbon oxides, and other gases.
- (2) Wastewaters consisting of the condensate, reactor wash waters, and cooling water.
- (3) Low-temperature heat.

The relative concentration of toxic impurities in the form of carbon monoxide and nitrogen oxides in the waste gases of ammonia manufacture is low, but even then special measures have to be devised so as to minimize the emissions. Toxic emissions can completely be avoided by resort to catalytic scrubbing in the presence of a reducing gas — this treatment reduces the nitrogen oxides of the waste gases to elemental nitrogen.

Due to the changeover to air cooling and the replacement of reciprocating compressors with turbocompressors, water consumption per tonne of NH₃ has been drastically reduced, and the amount of wastewaters discharged has been cut down by a factor of about 50.

The low-temperature heat of ammonia synthesis can be reclaimed by raising its thermal potential. This is done by adding an amount of high-

temperature heat. Unfortunately, conversion of waste heat to mechanical power in this way leads to a greater air pollution with flue gases.

An attractive way of reducing emissions and effluents from ammonia synthesis is to use a power cogeneration scheme incorporating a steam-gas cycle. Here, the process heat is supplied not only by the steam, but also by the products of fuel combustion.

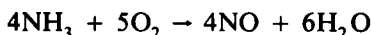
14.5 Nitric Acid Technology

Nitric acid is among the key tonnage products of the chemical process industries. In terms of production, it is second only to sulphuric acid. Nitric acid is widely used in the manufacture of many products used in industry and agriculture. Thus, close on 40% of the total production goes to make compound and nitrogen fertilizers, synthetic dyes, explosives, nitrodopes, plastics, synthetic drugs, and many other essential products.

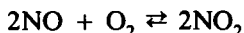
According to forecasts, the world's output of nitric acid will be 97.4 million tonnes in 1990 and 158 million tonnes in the year 2000. The expansion will mainly be achieved through the use of plants of large unit capacity and high-performance processes. It is hoped that a good deal will be contributed by the commercialization of biological and low-temperature fixation of atmospheric nitrogen.

Dilute nitric acid is manufactured in three stages as follows.

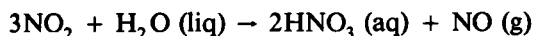
(1) Ammonia is directly oxidized with air to yield nitrogen oxide according to the reaction



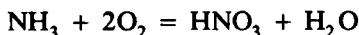
(2) The nitric oxide is further oxidized to nitric dioxide according to the scheme



(3) The nitrogen dioxide combines with water to form nitric acid



The overall reaction for the formation of nitric acid is



Raw materials for the manufacture of nitric acid. These include ammonia, air, and water.

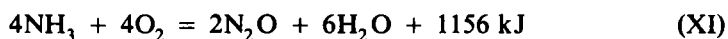
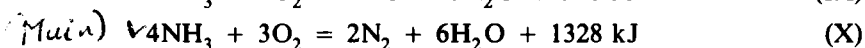
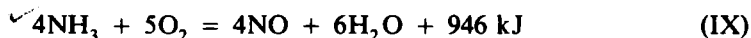
Ammonia. Synthetic ammonia carries varying amounts of impurities such as catalyst dust and lubricating oil (when reciprocating compressors are used at the compression step). Pure gaseous ammonia is obtained with the aid of liquid ammonia vaporizers and distillation units. The gaseous ammonia is further purified in filters made up of lentil-shaped elements

with high-pile cotton fabric as the filter medium. Fine impurities are removed by passing the ammonia-air mixture through a filter using foamed-plastic tubes.

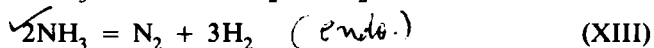
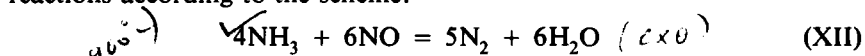
Air. Since it is taken within or near the plant's premises, atmospheric air is polluted with gases and dust. This air is thoroughly purified to remove the pollutants as they might otherwise poison the catalyst used in the ammonia oxidation step. As a rule, air is purified in a water-sprayed scrubber followed by a two-stage filter.

Water. Process water treatment includes settling to remove mechanical impurities, filtration, and chemical treatment to remove the dissolved salts. The production of reactive nitric acid calls for a pure steam condensate which is additionally treated for removal of likely impurities.

✓ **Physico-chemical foundations of ammonia conversion.** Without a catalyst, ammonia can directly be oxidized with atmospheric oxygen only to N_2 . When the oxidation is effected over a catalyst, the following parallel reactions take place between the ammonia and oxygen:



The above reactions may be accompanied by side (parallel or series) reactions according to the scheme:



The above equations describe the overall catalytic ammonia oxidation reaction and do not reflect the true mechanism of the process.

Table 14.3 lists the thermodynamic characteristics of the above reactions.

As is seen, of all the ammonia oxidation reactions, the one most feasible thermodynamically is reaction (X) involving the largest free energy change, ΔG . As the temperature is raised, the probability of reaction (IX) nearly doubles and that of reaction (X) remains almost unchanged.

The ammonia oxidation reactions are accompanied by a fall in free energy, and proceed at a high rate practically to completion (irreversibly). The heat of reaction is quite enough for the process to take place autothermally.

Ammonia oxidation catalysts should be highly specific, that is, they should speed up only one of the three likely reactions, namely reaction (IX) in which the ammonia is oxidized to nitrogen (II) oxide. The most specific

Table 14.3 Thermodynamic Characteristics of Ammonia Oxidation

Reaction	$\Delta H_{298},$ $\text{kJ mol}^{-1} \text{NH}_3$	$\Delta G, \text{kJ mol}^{-1}$ at temperature stated:		$\Delta S_{298},$ $\text{kJ mol}^{-1} \text{K}^{-1}$
		298K	1173K	
IX	-226.00	-246.21	-414.55	44.78
X	-317.20	-326.85	-335.22	32.44
XI	-276.11	-274.75	—	-4.67
XII	-452.62	-1814.80	-874.00	13.90
XIII	45.80	16.55	-82.54	103.16
XIV	90.310	-84.50	78.30	12.36

and active catalyst used for ammonia oxidation is a platinum-rhodium-palladium alloy.

Ammonia oxidation over a catalyst is a multi-stage heterogeneous process which takes place in the external diffusion region. The rate-controlling step of the process is the diffusion of ammonia to the surface of the catalyst. Several hypotheses have been advanced to explain the mechanism by which ammonia is oxidized over a platinum-based catalyst. They propose that as NH_3 is oxidized, unstable intermediates are formed — they finally break down and re-arrange to give nitrogen (II) oxide and elemental nitrogen.

The catalytic oxidation of ammonia according to reaction (IX) proceeds at a very high rate: In a matter of a few ten-thousandths of a second, 97-98% of the total ammonia is converted to nitrogen (II) oxide at atmospheric pressure and 95-96% at a pressure of 0.88-0.98 MPa. Given the same catalyst, the yield of nitrogen (II) oxide may be different, according to the operating conditions (temperature, pressure, linear velocity of the gas, ammonia content of the ammonia-air mixture, catalyst capacity, number of gauzes, etc.) chosen.

Influence of temperature. Temperature affects the yield of nitrogen (II) oxide most of all. A plot relating the yield of NO to temperature over a platinum catalyst is shown in Fig. 14.18. As the temperature is raised, the NO yield goes up — there is an optimal temperature (which is 900-920 °C for pure platinum) at which a maximum yield is achieved.

An important factor is the kindling temperature of the catalyst. This temperature depends mostly on the catalyst composition and less on the composition of the ammonia-air mixture. When the reaction is effected over a platinum catalyst, the oxidation of ammonia commences at 195 °C. A distinction of this reaction is that at first the ammonia is 'softly' oxidized to molecular nitrogen. An appreciable quantity of nitrogen (II) oxide appears at 300 °C. As the temperature keeps rising, the yield of nitrogen (II)

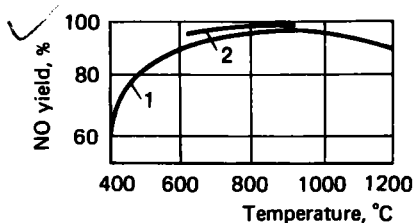


Fig. 14.18 Yield of nitrogen (II) oxide as a function of temperature:

1, one platinum gauze; 2, three Pt-Pd-Rh alloy gauzes

oxide increases to achieve a maximum figure of 96% over a pure platinum catalyst and 99% over a platinum-rhodium-palladium catalyst. Apart from the increase in the yield of nitrogen (II) oxide, the high process temperature offers some other advantages: the rate of ammonia oxidation is increased and the contact time is cut down*. For example, the increase in temperature from 650 °C to 900 °C cuts down the contact time from 5×10^{-4} to 1.1×10^{-4} s. Unfortunately, an increase in temperature entails an increased loss of the expensive platinum or, which is the same, the economic performance of the process is impaired. For the process to be effected economically, it should be conducted under the following conditions:

Pressure, MPa	0.1	0.304-0.51	0.71-1.011
Temperature, °C	780-800	850-870	880-920

As the temperature is raised from 780 °C to 850 °C, the direct loss of catalyst nearly doubles.

When choosing the temperature for ammonia oxidation, it is important also to consider the presence of impurities in the ammonia-air mixture. The temperature must be raised in proportion to the impurity content of the feedstock.

✓ *Influence of pressure.* As the process pressure rises, the yield of nitrogen (II) oxide falls off. This factor has been behind the delay in the commercialization of pressure nitric acid processes. On the other hand, the use of high pressure at the ammonia oxidation step makes it possible to increase the throughput of the plant and to use smaller-sized plant items. This consideration is gaining in importance now that there is a growing trend to build plants of an ever larger unit capacity. At state-of-the-art large nitric acid plants the ammonia oxidation step is effected at a pressure of 0.41-0.73 MPa.

The key factors for a high yield of NO to be obtained from the pressure processes is to operate them at a high temperature and at a longer contact time (with a greater number of catalyst gauzes).

* The contact time, that is, the span of time during which the reaction mixture is in contact with the catalyst gauze surface is inversely proportional to the volumetric flow rate of the ammonia-air mixture.

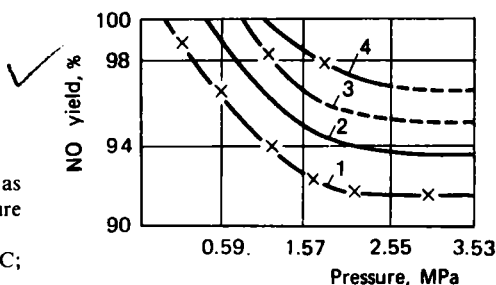
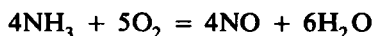


Fig. 14.19 Yield of nitrogen (II) oxide as a function of pressure and temperature at τ_{opt} :
1, 900 °C; 2, 950 °C; 3, 980 °C;
4, 1010 °C

As is seen from Fig. 14.19, for the yield of nitrogen (II) oxide to exceed 98% at a pressure of 0.41–0.71 MPa, the temperature must be in excess of 950 °C.

A higher pressure at the oxidation step means a higher linear velocity of the feed gas and a greater catalyst loading, and this is in turn related to an increase in the number of catalyst gauzes. It is seen from Fig. 14.20 that an increase in the number of catalyst gauzes leads to a higher conversion of the ammonia and a higher linear velocity of the gas. Obviously, the process pressure, linear velocity of the feed gas and the catalyst loading are intimately interrelated. Therefore, special care must be exercised in choosing them for the ammonia oxidation step if high yields of NO are to be obtained.

Influence of ammonia concentration. As has been noted, nitric acid is obtained by the direct oxidation of ammonia with air. Therefore, the NH_3 content of the ammonia-air feed depends on the oxygen content of the air. According to the reaction



it takes 1.25 moles of oxygen in order to completely oxidize 1 mole of ammonia. Hence, the maximum possible ammonia content of the ammonia-air feed is

$$[(21/1.25) \div (100 + 21/1.25)] \times 100 = 14.4 \text{ vol. \%}$$

Unfortunately with a 1.25:1 oxygen/ammonia ratio the NO yield does not exceed 60–80% even at atmospheric pressure. Also, with an ammonia content of 14.4% one would have to operate within the region of explosive concentrations. The lower limit of explosibility for an ammonia-air mixture at atmospheric pressure is 13.8 vol. % NH_3 . The limits of explosibility for ammonia-air mixtures are given in Fig. 14.21. As the $\text{O}_2:\text{NH}_3$ ratio rises to 1.7:1, which corresponds to a mixture carrying 11.5 vol. % ammonia, the NO yield increases. Any further increase in the $\text{O}_2:\text{NH}_3$ ratio by bringing down the ammonia content causes only slight changes in the yield of nitrogen (II) oxide.

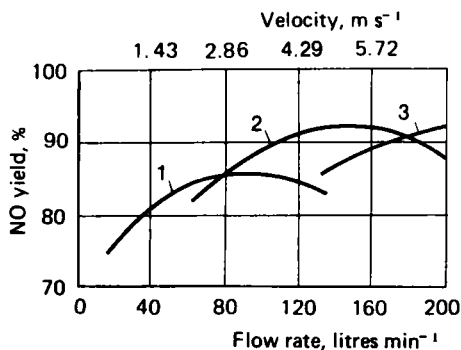


Fig. 14.20. NO yield as a function of gauze number and gas velocity at 1.96 MPa and 900 °C: 1, 10 gauzes; 2, 20 gauzes; 3, 50 gauzes

Thus, when atmospheric air is used for ammonia oxidation, the maximum possible ammonia content of the ammonia-air feed that gives a high NO yield is 11.0-11.5 vol. %, with an $O_2:NH_3$ ratio of 1.7:1 at a temperature of 870-920 °C. A plot of NO yield as a function of the $O_2:NH_3$ ratio of the feed is shown in Fig. 14.22. If the NO yield is to be high, there must be at least a 30% excess of oxygen over its stoichiometric quantity. This is because the surface of the platinum catalyst must always be covered by oxygen (in the absence of oxygen, ammonia would decompose with the evolution of H_2 and N_2 at a temperature as low as 400 °C).

Catalysts. That platinum outperforms all other catalysts in activity and specificity was shown by Ostwald in 1902. Characteristically, the activity towards ammonia oxidation is displayed by most metals and their alloys, but a high NO yield (upwards of 90%) can be achieved with only a very few of them.

While it has a high activity and specificity, platinum has a low kindling temperature (about 180 °C) and is both ductile and tough. Unfortunately, platinum is readily destroyed by elevated temperatures when exposed to high-velocity reactant streams and catalyst poisons. This causes losses of the expensive metal and a reduction in NO yield. These considerations have spurred the search for catalytically active alloys of platinum with other metals.

Industrial tests have proved the high stability of platinum catalysts with the addition of palladium and also catalysts made of the ternary Pt-Rh-Pd alloy. This has given impetus to the commercialization of such catalysts. In the USSR, the most commonly used ammonia oxidation catalysts today are Pt + 4 wt. % Pd + 3.5 wt. % Rh for use in atmospheric nitric acid plants and Pt + 7.5 wt. % Rh for use in pressure nitric acid plants.

The catalysts used for the direct oxidation of ammonia with air are in the form of a gauze made of wire. This form is convenient in use, entails low metal requirements, and is readily adaptable to simple ammonia oxidation vessels. In the USSR, catalyst gauzes are made of wire 0.09 mm in

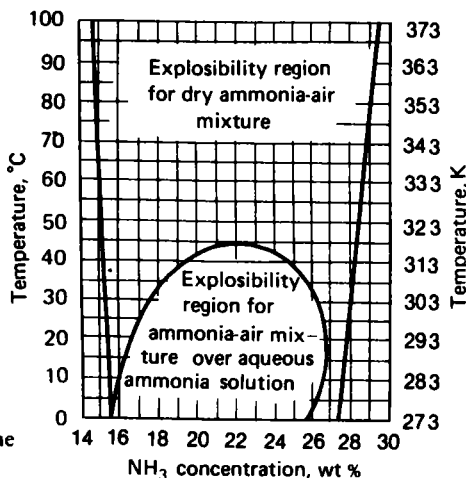


Fig. 14.21 Explosibility range of the ammonia-air mixture

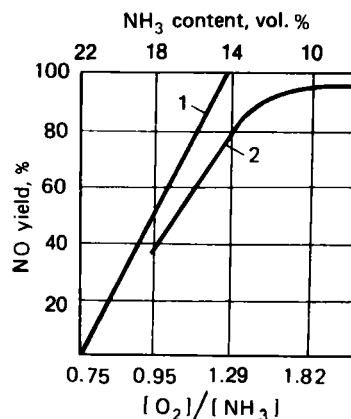


Fig. 14.22 NO yield as a function of the [O₂] : [NH₃] ratio in the ammonia-air mixture:

1, theoretical NO yield; 2, under actual conditions at 900 °C

diameter with 32 meshes to the centimetre and 1024 meshes to the square centimetre. Each mesh is 0.22 mm square.

Platinum-rhodium and platinum-rhodium-palladium catalysts are extremely sensitive to the impurities present in the ammonia and air. These impurities are phosphine, arsine, fluorine and its compounds, dichloroethane, mineral oils, acetylene, sulphur dioxide, hydrogen sulphide, and some others. The strongest catalyst poisons are the compounds of sulphur and fluorine. The impurities markedly degrade catalyst specificity and entail greater losses of platinum. For ammonia conversion to be maintained at a stable level, it is likewise important to treat the ammonia-air mixture for removal of mechanical impurities, notably the iron oxides and the dust that result from the ammonia synthesis iron

catalyst. The dust and iron oxides, if not properly removed, would be caught in the platinum catalyst gauzes and clog them, thereby reducing the area of contact between the catalyst and the feed gases and, in consequence, the level of ammonia oxidation.

The purity of the feedstocks used in the manufacture of nitric acid can be assured in two ways. One is to draw in air far away from the plant's site and the other is to use better systems for air and ammonia purification.

In the course of ammonia oxidation, the surface of the platinum gauzes becomes loose, and the elastic gauze wires are embrittled. This causes the gauze area to increase about 30-fold. At first, the activity of the catalyst goes up, but finally the gauzes are destroyed. Practice has shown that catalyst gauzes will last as much as 14 months in atmospheric processes and 8 to 9 months in processes effected at a pressure of 0.73 MPa.

Plant items used at the ammonia oxidation step. An ammonia oxidation unit operating at any pressure (Fig. 14.23) will usually include the following pieces of equipment: an air filter 1, a turbocompressor (air blower) 2 to compress and supply air, a mixer 3 often combined with a fine filter, an ammonia preheater 7, an air preheater 4, and an ammonia converter 5 along with a steam superheater and a waste heat boiler 6.

The key piece of equipment at this step is the contact converter, a plant item of complex design which has undergone many changes lately.

In sketch form, an atmospheric ammonia oxidation converter in which the ammonia-air mixture is fed from top is shown in Fig. 14.24. At the top of the converter is located a cardboard ammonia-air mixture fine filter, 2. The catalyst gauzes are supported by a bar screen below which there is a grid carrying a bed of metal rings, 5, which accumulate heat so as to accelerate the converter's start-up after a short break and also to catch coarse

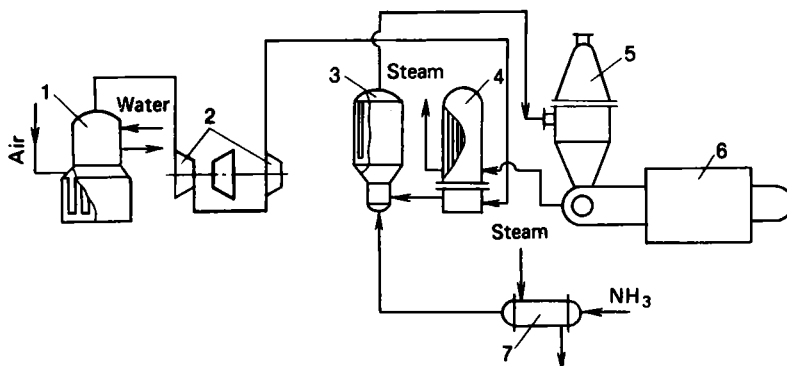


Fig. 14.23 Flowsheet of an ammonia oxidation unit:

1, filter; 2, turbocompressor; 3, mixer and fine filter; 4, air preheater; 5, converter; 6, waste-heat boiler; 7, ammonia preheater

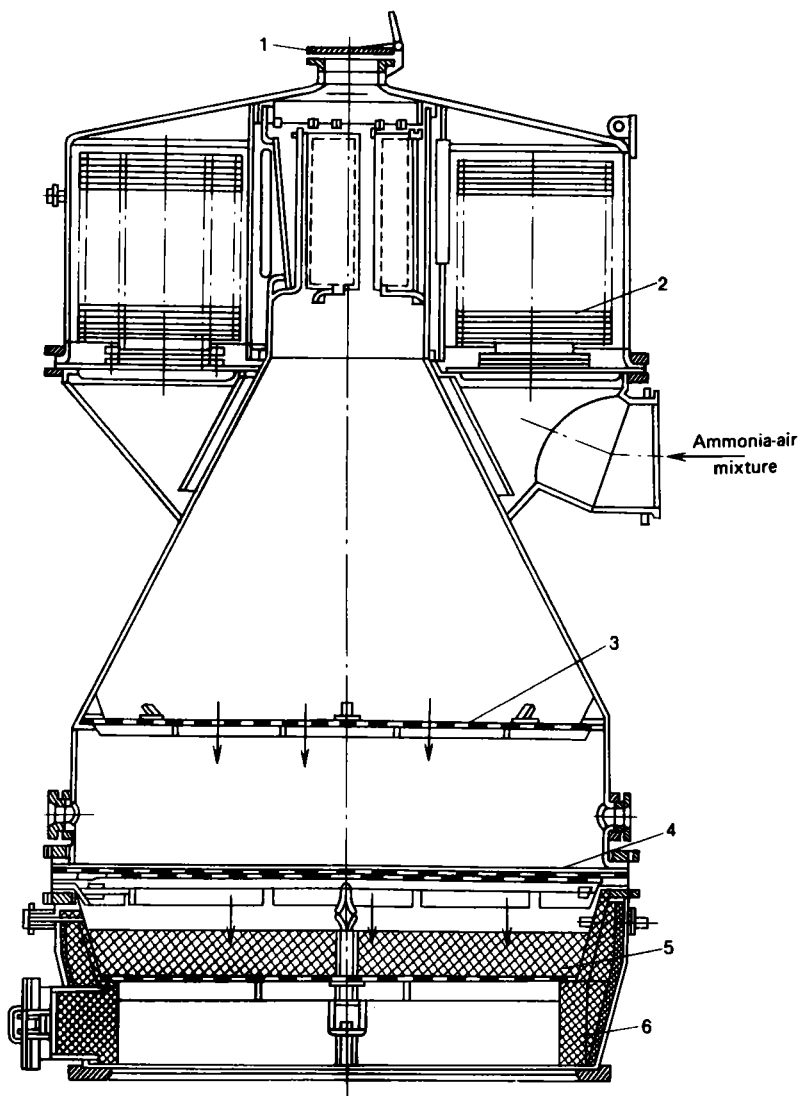


Fig. 14.24 Reactor combined with a cardboard filter:

1, blow-out disc; 2, cardboard filters; 3, distribution grid; 4, catalyst gauzes; 5, ring bed; 6, heat-resistant lining

platinum slivers entrained by the gas stream. The converter is set up atop a waste heat boiler. Its capacity is 48-50 t/d HNO_3 .

The loss of platinum is minimized by catching platinum dust and slivers and returning them to the catalyst preparation step. This is most often

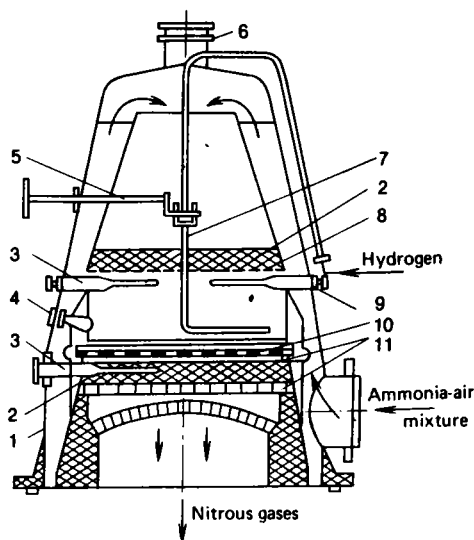


Fig. 14.25 Reactor:

1, shell; 2, Raschig rings; 3, thermocouples; 4, inspection window; 5, rotator; 6, blow-out disc; 7, catalyst preheating pipe; 8, distribution grid; 9, sampler; 10, catalyst gauzes; 11, bar screens

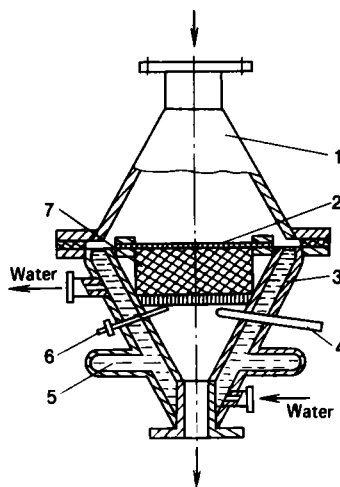


Fig. 14.26 Two-stage catalyst reactor operating at 0.54 MPa:

1, upper cone; 2, platinum gauze; 3, lower cone; 4, sampler; 5, water jacket; 6, thermocouple; 7, non-platinum catalyst

done by filtering the nitrous gases in a wide range of mechanical filters using various filter media. The filter medium most often used is continuous glass-fibre cloth. At this writing, calcium-oxide materials have been developed and tested for use in this capacity — they combine with platinum vapour chemically. With this form of platinum recovery, the sorbent is installed directly in the converter, back of the catalyst gauzes and is exposed to the conditions of the ammonia oxidation step. Platinum dust is recovered from the acid, from the sludge, and from the plant items and gas flues by rubbing their internal surfaces with hygroscopic cotton wool moistened in alcohol.

The combination of chemical recovery (with the calcium oxide paste) and conventional mechanical filters using fibrous materials as the filter media can recover as much as 85-90% platinum.

The converter shown in Fig. 14.25 is designed to oxidize ammonia to nitrogen oxide at a pressure of 0.73 MPa. It consists of an upper part in the form of a truncated cone 1.6-2.2 m in diameter and a lower cylindrical part. The 12 platinum catalyst gauzes are arranged in a holder which is located between the upper and lower sections of the vessel. The catalyst

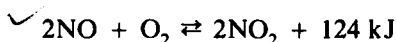
gauze holder is set up on a grid of concentric rings. The bar screen below them gives support to a bed of ceramic rings stacked up in regular tiers 20 cm high. This bed of rings catches some of the platinum and stabilizes the temperature at the catalyst gauzes.

The ammonia-air mixture enters the converter at a side, flows round in the upper cone, and enters the catalyst gauzes from above.

The top connection of the converter is covered with a blow-out disc designed to burst, should the pressure inside the converter suddenly rise to a critical value.

There is a more effective way of reducing platinum loss. How this is done in practice is illustrated in Fig. 14.26. The figure shows a converter operating at a pressure of 0.54 MPa and using a two-stage catalyst arrangement. The first stage uses platinum-based gauzes and the second stage, a non-platinum catalyst held in a high-temperature steel basket. One of the best non-platinum catalysts is an iron-chromium type. The ribs welded to the vessel's shell give support to a high-temperature bar screen which carries Ni-Cr gauzes. The gauzes bridge the clearance between the shell and the basket and prevent the ammonia from short-circuiting across the converter and the catalyst pellets from being entrained by the gas stream.

Oxidation of nitrogen (II) oxide. The nitrous gases resulting from ammonia oxidation include nitrogen (II) oxide, nitrogen, oxygen, and water vapour. The next step in the manufacture of nitric acid is the oxidation of nitrogen (II) oxide to nitrogen dioxide. The reaction goes on according to the scheme



This is a reversible reaction which proceeds with a reduction in volume and liberates heat. Hence, in agreement with Le Chatelier's principle, these conditions — the fall in temperature and the rise in pressure — cause the reaction equilibrium to shift to the right, that is, towards the formation of NO_2 . The equilibrium constant of the oxidation reaction

$$K_p = p_{\text{NO}_2, e}^2 / (p_{\text{O}_2, e} p_{\text{NO}, e}^2)$$

for several values of temperature is this:

$t, ^\circ\text{C}$	20	100	200	300	500	700	900
K_p	1.24×10^{13}	1.82×10^7	7.41×10^3	45.5	8.5×10^{-2}	2.12×10^{-3}	1.51×10^{-4}

It is seen that at temperatures not over 100 °C the reaction proceeds almost completely towards the formation of NO_2 . At higher temperatures, the equilibrium is shifted to the left, and at over 700 °C practically no nitrogen dioxide is formed. Because of this, the nitrous gases leaving the converter do not carry NO_2 , and in order to obtain it, the gas mixture must be cooled

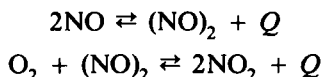
to below 100 °C. The oxidation of nitrogen (II) oxide is the slowest step in the manufacture of nitric acid. Its rate determines the overall rate of the process.

The rate of the oxidation reaction may be written thus

$$w_r = kp_{\text{NO}}^2 p_{\text{O}_2} \quad (14.8)$$

It 'strongly depends on the reactant concentrations, pressure and temperature. The rate at which NO is converted to NO₂ can be raised by increasing the NO content of the feed through the use of oxygen-enriched air or pure oxygen for ammonia oxidation.

The rate at which NO is oxidized to NO₂ increases with decreasing temperature, whereas an increase in temperature slows it down to a point where it ceases almost completely. Several hypotheses have been advanced to explain the phenomenon. The one most widely held consists in that the oxidation of NO to NO₂ proceeds via the formation of an intermediate, that is, a dimer of nitrogen (II) oxide:

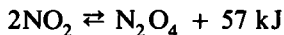


The formation of the NO dimer is a reversible process which liberates heat. In consequence, the rise in temperature is bound to shift the equilibrium of this reaction to the left. As a corollary, the equilibrium constant will decrease and the equilibrium concentration of the dimer in the gas mixture will go down. The rate at which the dimer is further oxidized to the dioxide

$$dn_{\text{NO}_2}/d\tau = k_1 p_{(\text{NO})_2} p_{\text{O}_2} \quad (14.9)$$

depends on the dimer concentration $p_{(\text{NO})_2}$. To sum up, the slow-down in the oxidation of nitrogen oxide to nitrogen dioxide may be explained by the fact that a rise in temperature brings about a heavy fall in the dimer concentration.

In atmospheric nitric acid plants, around 92% of the NO is oxidized. The remaining NO is absorbed (along with the NO₂) by an alkali because the complete oxidation would have needed too much time and prohibitively large pieces of equipment. As a rule, the nitrous gases are worked into the dilute acid at a temperature of 10-50 °C. At these temperatures some of the nitrogen dioxide is polymerized into N₂O₄:



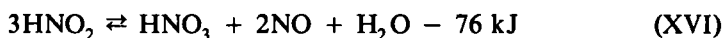
The relation between the polymerization of NO₂ and temperature is this:

<i>t</i> , °C	200	100	70	30	0	-20
Percent polymerization	0.7	2.5	38	77.8	89	92

The polymerization of NO_2 proceeds at a very high rate. Therefore, the $\text{NO}_2:\text{N}_2\text{O}_4$ ratio at any time is determined by the conditions of equilibrium which is established practically instantaneously. Since the reaction entails a reduction in volume, the rise in pressure favours the formation of N_2O_4 .

The nitrous gases entering the absorption step include NO_2 , N_2O_4 , NO , N_2O , N_2 , N_2O_3 , and water vapour.

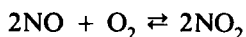
Absorption of nitrogen dioxide. The absorption of nitrogen oxides by water entails the dissolution of NO_2 , N_2O_4 and N_2O_3 with the formation of nitric and nitrous acids. Since it is a compound of low stability, the nitrous acid decomposes into nitric acid, nitrogen (II) oxide, and water. The absorption proceeds according to the scheme



The overall equation describing the interaction of NO_2 with water may be written thus:



which provides the basis for all computations in the analysis and design of the absorption step. It follows from this equation that 3 moles of NO_2 produce 2 moles of HNO_3 and 1 mole of NO which is again oxidized to NO_2 :



It may be hypothesized that dilute nitric acid is formed by the following mechanism. The NO_2 and N_2O_4 of the gas phase are always in a state of chemical equilibrium and their transport to the interface is governed by the molecular diffusion of gases. At the gas-liquid interface, the NO_2 passes into the liquid phase. After the NO_2 is dissolved, reaction (XV) takes place and proceeds at a relatively high rate in comparison with the diffusion step.

Following that, the nitrous acid in the liquid phase is decomposed at a relatively low rate according to reaction (XVI). The NO thus formed is partly oxidized in solution, but its greater proportion reacts with oxygen in the gas phase according to reaction (XVII). The absorption and the chemical reactions that take place in solution are accompanied in part by the same reactions in the gas phase that result in the formation of nitric acid.

The slowest step that controls the rate of absorption of the nitrogen oxides is their diffusion into the liquid phase. When the nitrogen dioxide reacts with water vapour, an acid mist is produced in the gas phase, and this presents an increased opposition to the absorption of nitrogen oxides.

The absorption of nitrogen dioxide by aqueous solutions of nitric acid depends on temperature, pressure, and acid concentration. As the

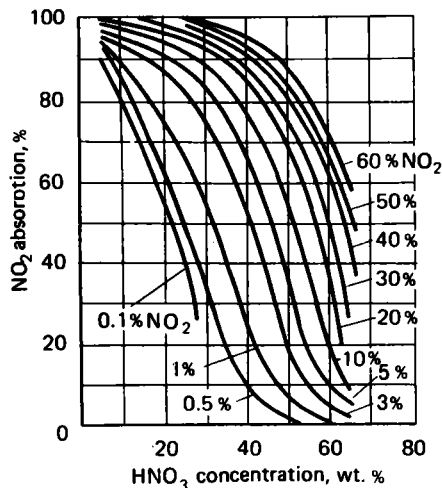


Fig. 14.27 Nitrogen dioxide absorption as a function of nitric acid concentration at equilibrium, a temperature of 35 °C and a total gas pressure of 0.1 MPa

temperature and acid concentration are brought down and the pressure is raised, the conversion of nitrogen dioxide goes up. The absorption nearly ceases when the concentration of nitric acid exceeds 65%. Figure 14.27 shows an equilibrium diagram for the absorption of NO_2 by nitric acid solutions. It is seen that the concentration of the resultant nitric acid depends on the conditions under which NO_2 is in equilibrium over the nitric acid.

It is to be noted that the extent to which NO is oxidized to NO_2 depends on the free volume and the quantity of absorbed nitrogen oxides on the interfacial area between the gas and liquid. Therefore, one of the key requirements that an absorber is expected to meet is provision of a maximum free volume and an extended absorption surface area.

The absorbers used in the commercial manufacture of nitric acid are the bubble-cap type, the sieve-tray type, and the over-flow type. A bubble-cap tower with two interfacial zones, designed to operate as a nitrous gas absorber, is shown in Fig. 14.28.

Pressure nitric acid plant. In the Soviet Union, the first plant in this category was designed in 1960s. It has a capacity of 120 thousand t/yr HNO_3 and operates at a pressure of 0.73 MPa. The waste gases are scrubbed by a high-temperature catalytic process, and the product HNO_3 is 53-58% strong. A simplified flow-sheet of this plant is shown in Fig. 14.29.

Atmospheric air is thoroughly purified in a two-stage filter 1 (the first stage uses a Soviet brand of Terylene and the second, Petryanov cloth). The purified air is compressed by a two-stage air compressor. The first stage, 18, compresses the air to 0.35 MPa. Due to adiabatic compression, the air is at the same time heated to 165-175 °C. After cooling, the air is

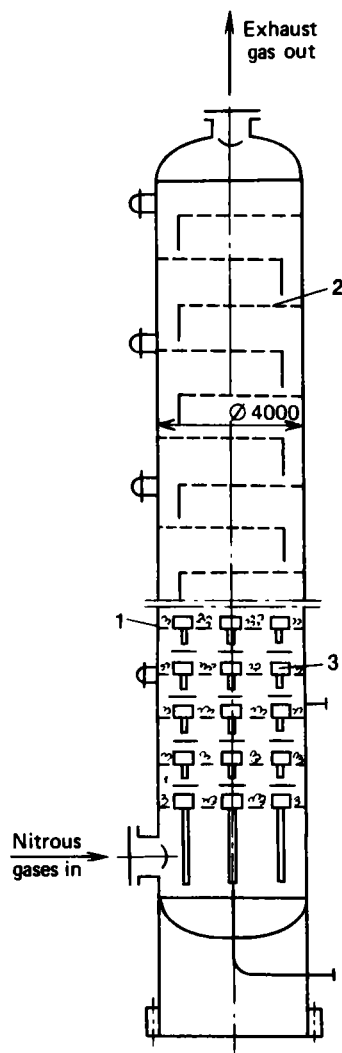


Fig. 14.28 Nitrous gas absorption tower of the AK-72 nitric acid unit:

1, shell; 2, sieve plate; 3, double-interface plate

routed to the second compression stage, 16, where its pressure is raised to 0.73 MPa.

The main body of the air stream after compression is raised to 250-270 °C in an air preheater 12 which reclaims the heat of the nitrous gases, and is passed to a mixer 6 to be mixed with ammonia.

The gaseous ammonia produced by vaporizing liquid ammonia is scrubbed to remove moisture, lubricating oil and catalyst dust, is passed through a preheater 5 where it is raised to 150 °C, and finally goes to mixer

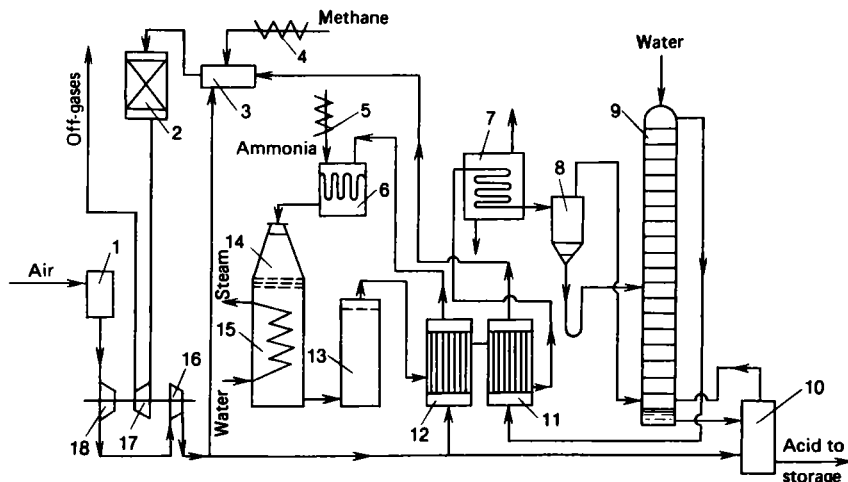


Fig. 14.29 Flowsheet of a 0.73 MPa nitric acid producing unit with a compressor driven by a gas turbine:

1, air filter; 2, catalytic scrubbing unit; 3, combustor; 4, methane preheater; 5, ammonia preheater; 6, ammonia-air mixer and foamed-plastic filter; 7, cooler-condenser; 8, separator; 9, absorption tower; 10, bleaching tower; 11, tail-gas preheater; 12, air preheater; 13, nitrous-gas oxidizer; 14, reactor; 15, waste-heat boiler; 16, turbocompressor stage; 17, gas turbine; 18, turbocompressor stage

6. The mixer is combined in a common shell with a foamed-plastic filter. After purification, the ammonia-air mixture with an NH_3 content of not over 10% by volume is passed to a converter, 14, for oxidation.

In the converter, the ammonia is oxidized with air over platinum-rhodium catalyst gauzes at 870-900 °C. The degree of conversion is 96%. The nitrous gases at 890-910 °C are passed to a waste-heat boiler 15 set up below the converter. In the boiler the nitrous gases give up their heat so that they are cooled to 170 °C, and this heat causes the chemically purified and deaerated boiler feedwater to boil. This produces steam at a pressure of 1.5 MPa and a temperature of 230 °C, which goes to services.

Downstream from the waste-heat boiler, the nitrous gases enter a nitrous-gas oxidizer 13 which is a hollow vessel with a glass-cloth filter at the top to catch platinum catalyst dust. Some of the nitrous gases (about 40% by volume) are oxidized in the waste-heat boiler. In oxidizer 13, the proportion is raised to 85%. Owing to the heat of oxidation, the nitrous gases are raised to 300-335 °C. This heat is reclaimed in air preheater 12. Cooled in this preheater, the nitrous gases are passed to a preheater, 11, where they are further cooled to 150 °C and heat the tail gas to 110-125 °C. Then the nitrous gases are routed to a cooler-condenser, 7, cooled with recycled water. This causes the water vapour to condense and a

weak nitric acid to form. The nitrous gases carrying the weak nitric acid enter a separator, 8, to give up the nitric acid which is then fed to the 6th-7th plate of an absorption tower, 9. The nitrous gases are fed into the tower beneath the lowermost plate, whereas the cooled steam condensate enters the tower at the top. The weak nitric acid thus formed flows down the tower to the lower plates. The concentration of the nitric acid is gradually increased as it absorbs more nitrogen oxides so that at the exit the acid is 55-58% strong and carries about 1% by volume dissolved nitrogen oxides. Therefore, the acid is passed to a bleaching tower, 10, where hot air is blown through the contents to remove the nitrogen oxides, and the bleached acid is transferred to storage. The air leaving the bleaching tower enters the lower part of absorption tower 9.

As much as 99% of the nitrogen oxides is thus absorbed. The tail gas leaves the absorption tower at a temperature of 35 °C and carries around 0.11% by volume nitrogen oxides. It is then passed through a preheater, 11, where it is raised to 110-145 °C and fed to the combustor, 3, of a catalytic gas scrubber. Here the tail gas is raised to 390-450 °C by burning natural gas preheated in a preheater, 4. From the combustor the tail gas is routed to a double-bed catalytic scrubbing unit, 2. The first bed is aluminium oxide with a coat of palladium, and the second bed is aluminium oxide. Catalytic scrubbing takes place at a temperature of 760 °C. The purified gas enters a gas turbine, 17, at a temperature of 690-700 °C, and the power reclaimed by the turbine from the heat of the tail gas is used to drive a turbocompressor, 18. Next, the gas is routed to a waste-heat boiler and an economizer (not shown in the diagram) and is finally discharged to the atmosphere. The nitrogen oxide content of the exhaust gas is 0.005-0.008% by volume, and the CO₂ content, 0.23% by volume.

As is seen, the plant is fully self-supporting in terms of energy which is reclaimed by the gas turbine mounted on a common shaft with the turbocompressor.

The AK-72 process for the manufacture of nitric acid. This process developed in the Soviet Union has at its basis a closed-cycle power cogeneration scheme which includes two ammonia oxidation steps, cooling of the nitrous gases at a pressure of 0.42-0.47 MPa, and nitrogen oxide absorption at a pressure of 1.1-1.26 MPa. The product nitric acid is 60% strong. The first 380 thousand t/yr HNO₃ plant using the AK-72 process was put on stream in 1976.

The process flowsheet is shown in Fig. 14.30. Air is drawn in through an air-scoop funnel, 25, purified to remove dust in a filter, 24, compressed by an air compressor, 23, to a pressure of 0.42 MPa, and divided into two streams one of which goes to a converter and the other to an ammonia

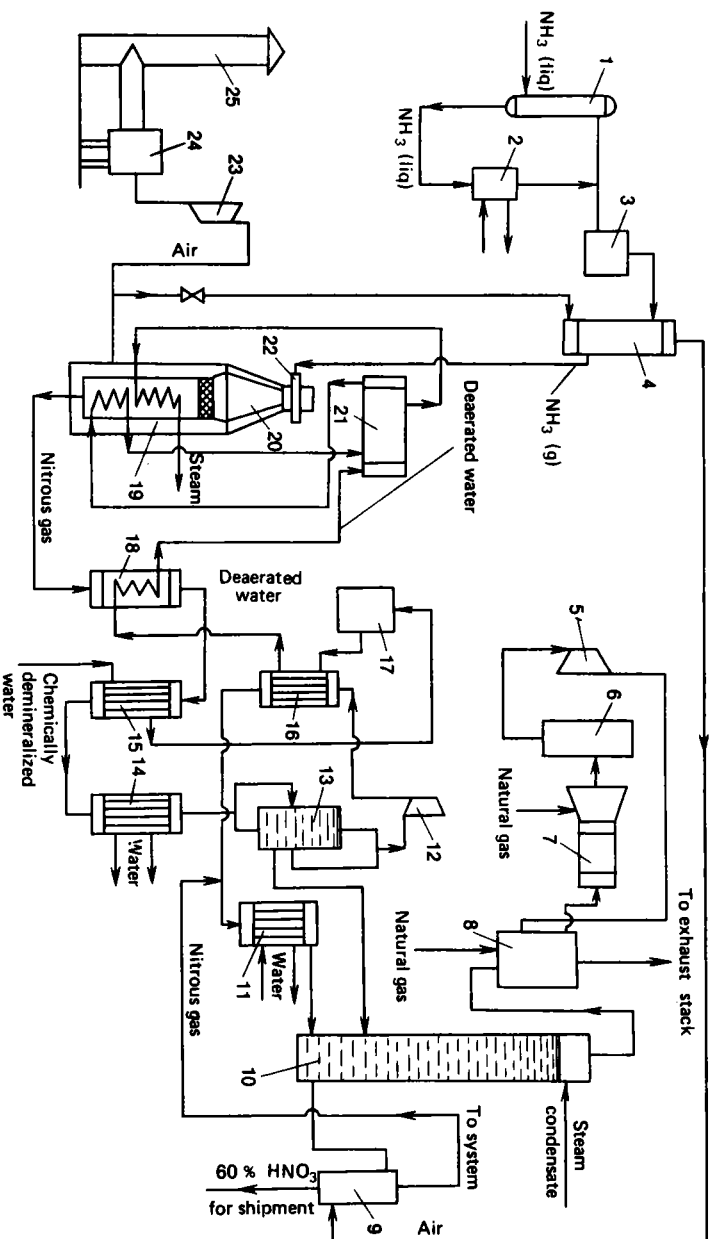


Fig. 14.30 Process flowsheet of the AK-72 nitric acid plant:

1, receiver; 2, vaporizer; 3, filter; 4, ammonia preheater; 5, power-recovery turbine; 6, catalytic scrubbing unit; 7, mixer; 8, combustor; 9, bleaching tower; 10, absorption tower; 11, water cooler; 12, air compressor; 13, gas scrubber; 14, water cooler; 15, heat exchanger; 16, deaeration tower; 18, economizer; 19, waste-heat boiler; 20, converter; 21, drum separator; 22, mixing chamber; 23, air-scoop funnel

preheater. Liquid ammonia (a vapour-liquid mixture) is routed via a receiver, 1, to a vaporizer, 2, where it evaporates at a temperature of 10-16 °C and a pressure of 0.6 MPa. Following the vaporizer, the gaseous ammonia is treated for removal of lubricating oil and mechanical impurities in a filter, 3, and goes to an ammonia preheater, 4, where it is raised to a temperature of 80-120 °C by hot air.

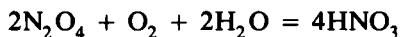
The purified air and ammonia enter the mixing chamber, 22, of the converter, 20. The resultant ammonia-air mixture contains 9.6-10.0% by volume NH_3 . Following a fine filter built into the converter, the ammonia-air mixture passes through the two-stage catalyst unit consisting of three platinum-based gauzes and a bed of a non-platinum catalyst. The nitrous gases at 840-860 °C enter a waste-heat boiler, 19, installed below the converter, where they are cooled to generate steam at a pressure of 40 MPa and a temperature of 440 °C. The boiler feedwater is chemically purified and deaerated in a tower, 17. The deaerated water is passed through a heat exchanger, 16, where it is raised to 150 °C by the nitrous gases, and an economizer, 18, whence it goes to the drum, 21, of the waste-heat boiler.

On leaving the waste-heat boiler, the nitrous gases are cooled in economizer 18, give up their heat in preheater 15, and enter water cooler 14 for further cooling to 55 °C. As the nitrous gases are cooled, the water vapour is condensed to give 40-45% nitric acid which is passed on to a gas scrubber, 13, which also receives the nitrous gases. In the scrubber, removal of nitrite and nitrate salts is accompanied by cooling and a further condensation of nitric acid. The acid emerging from the lower part of the scrubber goes to absorption tower 10, and the nitrous gases are compressed to 11-12.6 MPa in a compressor, 12. As they are compressed, the gases rise to a temperature of 210-230 °C. Following the compression step, the nitrous gases are cooled to 155-165 °C in heat exchanger 16, and to 60-65 °C in a second-stage cooler, 11, and passed on to absorption tower 10. The tower plates carry coils to cool the acid. At the top, the tower receives steam condensate (H_2O) at a temperature of not over 40 °C. The product nitric acid 58-60% strong is withdrawn at the base of the tower. It goes to a bleaching tower, 9, where it is blown to remove the dissolved nitrogen oxides and is then passed to storage.

The tail gas from the absorption tower is heated in a combustor, 8, mixed with natural gas in a mixer, 7, and routed at a temperature of 480 °C to unit 6 which effects catalytic scrubbing to remove the nitrogen oxides. The catalytic scrubber uses a palladium catalyst on an alumina base. Following the catalytic decomposition, the tail gas carrying up to 0.008% by volume nitrogen oxides at a temperature of 750 °C enters a power recovery turbine, 5, which is part of a gas-turbine unit. Here the heat of the tail gas is converted to mechanical power and the gas pressure is at the same time

brought down to 0.95-1.05 MPa. The power generated by the gas turbine is utilized to drive the nitrous-gas and air compressors, 12 and 23.

Manufacture of high-strength nitric acid. *Direct synthesis of HNO_3 from nitrogen oxides.* This process is based on the reaction of liquid nitrogen oxides with water and gaseous oxygen at a pressure of 5 MPa according to the scheme



Given a concentration of 100%, all of the nitrogen dioxide would become a liquid at atmospheric pressure and a temperature of 21.5 °C. When, however, the NO produced by ammonia oxidation is further oxidized to nitrogen dioxide, the NO_2 content of the feed is just about 11% by volume. There is no way of turning this NO_2 to liquid at the concentration stated and at atmospheric pressure. This is the reason why high pressure has to be employed in order to liquefy nitrogen oxides.

The degree of liquefaction of NO_2 as a function of pressure and temperature is given in Table 14.4.

As is seen, a nitrous gas carrying 10% NO_2 cannot be fully liquefied even at elevated pressure and a temperature as low as -20 °C. Therefore it is customary in the manufacture of high-strength nitric acid to liquefy nitrogen dioxide by a process based on the dissolution of NO_2 in concentrated nitric acid. Concentrated nitric acid absorbs NO_2 from dilute nitrous gases with the formation of nitrooleum which answers the general formula $\text{HNO}_3 \cdot \text{NO}_2$. On decomposing, it leaves 98% nitric acid (the product) and concentrated nitrogen dioxide which is liquefied by a two-stage cooling process. The first stage uses water, and the second, a brine at a temperature in the range from -7 to -10 °C. If it were cooled below -10 °C, the nitrogen dioxide would turn solid and might clog the cooler tubes.

In oxidation towers, the nitrogen oxide cannot be fully oxidized to NO_2 . Therefore, the feed is further oxidized in a separate packed tower us-

**Table 14.4 Degree of Liquefaction of NO_2 (% by volume)
(with the gas phase containing 10% by volume NO_2)**

Gas pressure, MPa	Degree of liquefaction, % vol., at temperature stated, °C			
	+ 5	- 3	- 10	- 20
1.0	33.12	56.10	72.90	84.49
0.8	16.61	44.74	66.18	80.54
0.5	—	9.75	45.10	68.59

ing concentrated nitric acid according to the reaction



This raises the conversion of NO to NO₂ to as high as 98-99%, but the original concentrated nitric acid is at the same time diluted to 70-75% by weight.

The liquid nitrogen oxides thus obtained react with the dilute nitric acid and, acted upon by oxygen at a pressure of 5 MPa and a temperature of 80 °C, form high-strength nitric acid.

Concentration of nitric acid with dehydrating agents. The dilute nitric acid made by conventional processes cannot be concentrated by simple distillation because a constant boiling (azeotropic) mixture is formed which contains 68.4% HNO₃ by weight.

In commercial practice it is customary to use a dehydrating agent to aid in removal of the water. The dehydrating agents most commonly used industrially include concentrated sulphuric acid, phosphoric acid, concentrated solutions of nitrates, and some others. Treatment with a dehydrating agent brings down the concentration of water vapour over the boiling mixture and raises the proportion of nitric acid vapour which, on condensing, gives 98% HNO₃.

The flowsheet for the concentration of nitric acid with sulphuric acid is shown in Fig. 14.31. There is a pressure tank, 1, which feeds dilute nitric acid into a concentration tower, 6, via two monitor vessels 2 connected in parallel. One acid stream is passed to a vaporizer, 3, and is fed as a mixture of liquid and vapour to the 10th plate of tower 6, and the other stream goes without preheat to a higher plate.

Another pressure tank, 4, supplies sulphuric acid via a flow regulator, 5, to the top of tower 6 above the inlet for the cold stream of nitric acid. The live stream entering the tower at the base heats the ternary mixture, thus causing the nitric acid to vaporize. The nitric acid vapour raised to 70-85 °C flows upwards, leaves by a port in the tower roof, and enters a cooler-condenser, 7. This vapour carries nitrogen oxides and water as impurities. In the cooler-condenser, the nitric acid vapour condenses at about 30 °C to give 98-99% HNO₃, and some of the nitrogen oxides are absorbed by this acid. The concentrated nitric acid carrying an amount of nitrogen oxides is routed to the two top plates of the tower, passes them consecutively, and the nitrogen oxides are purged with the nitric acid vapour entering condenser 7. The uncondensed nitric acid vapour and the separated nitrogen oxides are routed to a water-sprayed absorption tower, 10. The 50% nitric acid thus obtained is passed to a collector, 11, and again goes for concentration. After cooling, the concentrated nitric acid goes to storage. The spent sulphuric acid carrying 65-68% H₂SO₄ is re-concentrated for further use.

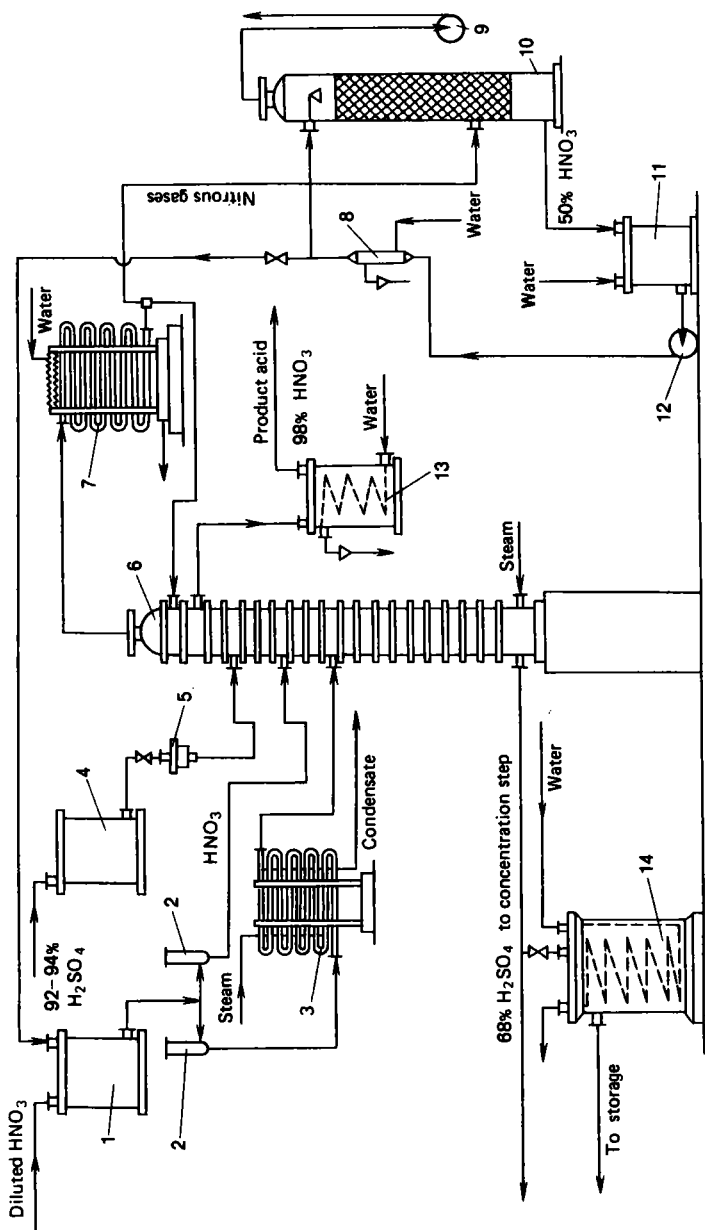


Fig. 14.31 Flowchart for the concentration of dilute nitric acid with sulphuric acid:
 1, nitric-acid pressure tank; 2, monitor vessel; 3, dilute nitric acid vaporizer; 4, sulphuric acid pressure tank; 5, acid flow regulator; 6, concentration tower; 7, cooler-condenser; 8, circulating-acid cooler; 9, fan; 10, absorption tower; 11, collector; 12, pump; 13, concentrated nitric acid cooler; 14, spent sulphuric acid cooler

vapour is then passed to a condenser, 4, whence some of it is returned to the distillation tower as reflux, and the remainder goes to storage. The 75% nitric acid collected at the base of the distillation tower flows to the stripping tower. The solution containing 55-70% magnesium nitrate withdrawn at the base of the stripping tower is reconcentrated in a reboiler, 8, and a vacuum vaporizer, 7, to a 80% solution of $\text{Mg}(\text{NO}_3)_2$, and recirculated to the stripping tower.

Environmental pollution abatement in the manufacture of nitric acid.

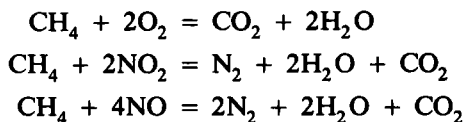
As more nitric acid is manufactured, there is a steady increase in the volume of waste gases and, in consequence, in the quantity of nitrogen oxides discharged to the atmosphere. Nitrogen oxides are detrimental to any form of life. Some plants suffer damage after one hour of exposure to an atmosphere containing 1 mg of the oxides per cubic metre of air. Nitrogen oxides cause irritation to the mucous membranes of the respiratory tract, impair oxygen supply to tissue, and entail other untoward consequences.

The tail gas leaving the absorption towers in the manufacture of nitric acid carries from 0.05 to 0.2% by volume nitrogen oxides. For this reason, as is required by relevant sanitary regulations, it must be suitably treated before its discharge to the atmosphere.

A radical solution to the problem of tail gas purification is offered by the catalytic reduction of nitrogen oxides with the combustible gases hydrogen, natural gas, carbon monoxide, and ammonia. The choice of the operating conditions for the catalyst and of its type depends on the combustible gas used. The reduction of nitrogen oxides brings down their content in the purified gas to 0.001-0.005% by volume. This is in keeping with applicable sanitary standards for the content of nitrogen oxides in the near-ground layer of air for plants of 1 million t/yr HNO_3 capacity concentrated in a single community and with emissions discharged at an altitude of 100-150 m.

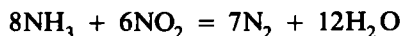
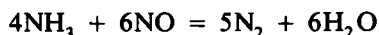
Some plants producing nitric acid by a pressure process purify their tail gas with natural gas as oxidizer and palladium as catalyst on alumina as its base.

The following reactions take place over the catalyst:



As a result of this treatment, the tail gas carries as little as 0.005% by volume nitrogen oxides. The heat of reaction is reclaimed to raise steam. The treatment is an integral step of nitric acid manufacture and has been incorporated in the 0.73 MPa and AK-72 processes in the Soviet Union.

When ammonia is used as the oxidizer, it reacts over an alumina-vanadium catalyst with only nitrogen oxides, thereby providing for selective reduction according to the reactions



A feasible way to remove nitrogen oxides from the tail gas to a level compatible with relevant safety standards as regards their concentration in the near-ground layer of air after discharge from a stack is an adsorption-desorption process which uses a continuously circulating sorbent (silica gel). Still other processes use adsorption on zeolites (molecular sieves), scrubbing with an acid solution of urea, and other wash liquors.

State-of-the-art nitric acid plants do not discharge their wastewater to sewers. Although they use large quantities of cooling water, it is continuously recirculated. The liquors periodically discharged from pumps and other pieces of equipment, such as during repair, are collected in ponds and neutralized.

Chapter Fifteen

SULPHURIC ACID AND FERTILIZER TECHNOLOGY

The manufacture of sulphuric acid and fertilizers ranks high among the chemical process industries along with the production of nitrogen compounds. In fact, these two complexes are closely related because sulphuric acid, ammonia, and nitric acid are the key components of feedstocks for the manufacture of fertilizers.

15.1 Sulphuric Acid Technology

In terms of production and usage, sulphuric acid leads all the other inorganic acids produced by the chemical process industries. At this writing, its world production totals about 150 million tonnes per year (against about 50 million tonnes of nitric acid). This above all is because sulphuric acid is among the strongest and cheapest acids. It does not fume; when concentrated, it does not attack iron and steels; and it remains liquid over a wide range of temperature — from $-40\text{ }^{\circ}\text{C}$ to $260\text{--}336.5\text{ }^{\circ}\text{C}$.

Sulphuric acid has found many and diverse uses. A substantial part of its production is used as a semi-product in many chemical industries, such as the manufacture of fertilizers, salts, acids, and explosives. It is also used in the manufacture of dyes, chemical fibres, metals, textiles, food, etc.

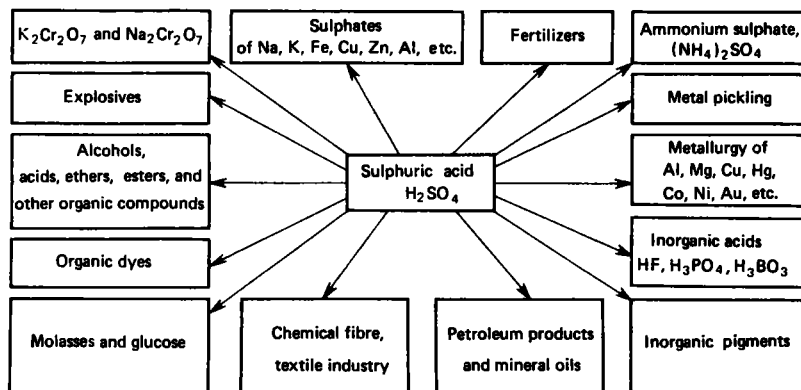


Fig. 15.1 Applications of sulphuric acid

Sulphuric acid can exist as H_2SO_4 and as a compound with water: $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, and with sulphur trioxide: $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ and $\text{H}_2\text{SO}_4 \cdot 2\text{SO}_3$.

In industry, the name 'sulphuric acid' can mean both its anhydrous form, H_2SO_4 , its aqueous solutions (actually, they are mixtures of H_2O , H_2SO_4 and the compounds $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$), and solutions of sulphur trioxide in anhydrous sulphuric acid, also called 'oleum' (a mixture of H_2SO_4 and the compounds $\text{H}_2\text{SO}_4 \cdot m\text{SO}_3$).

Anhydrous sulphuric acid is a heavy, oily and colourless liquid which can mix with water and sulphur trioxide in any ratio. The density, crystallization or freezing point, boiling point and some other physical properties of sulphuric acid depend on its composition. The crystallization diagram of an $\text{H}_2\text{O}-\text{H}_2\text{SO}_4-\text{SO}_3$ system is shown in Fig. 15.2. The peaks on this diagram represent compounds which answer the general formulas $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ or $\text{H}_2\text{SO}_4 \cdot m\text{SO}_3$, and the minima owe their existence to the fact that a mixture of two substances crystallizes at a lower temperature than does any of the constituents.

Anhydrous 100% sulphuric acid crystallizes at a relatively high temperature of 10.7°C . To prevent the product from freezing in transit and storage, the concentration of commercial sulphuric acid is chosen such that its freezing point is sufficiently low. In the USSR, sulphuric acid is marketed in three grades as follows.

	Concentration	Freezing point, $^\circ\text{C}$
Tower acid	75%	-29.5
Contact-process acid	92.5%	-22.0
Oleum	20% free SO_3	+2

A plot relating the boiling point of sulphuric acid to its composition at atmospheric pressure is shown in Fig. 15.3. The lower curve in this

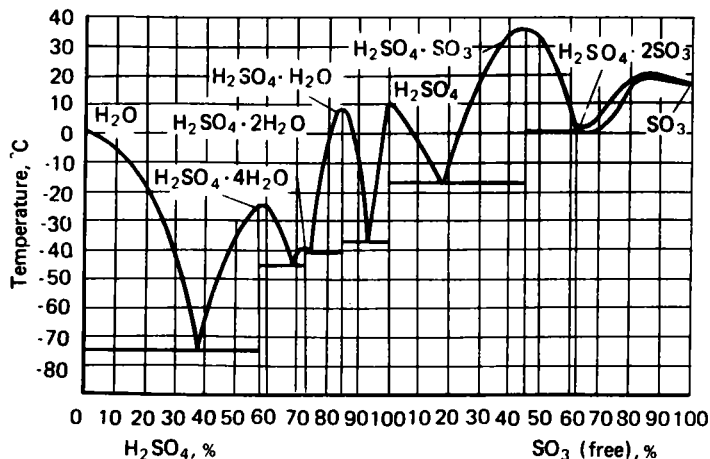


Fig. 15.2 Crystallization (freezing) point of sulphuric acid

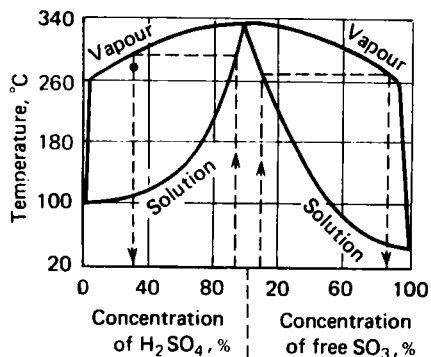


Fig. 15.3 Boiling point of sulphuric acid at atmospheric pressure

equilibrium diagram represents the composition of the liquid phase, and the upper curve, the composition of the vapour phase in equilibrium with the boiling liquid. As is seen, sulphuric acid and water form an azeotropic mixture which is 98.3% H_2SO_4 and 1.7% H_2O , with a maximum boiling point (336.5 °C). In the case of the acid having an azeotropic concentration, the liquid and vapour phases in equilibrium with each other have the same composition. In the case of a more dilute acid, the vapour phase is high in water vapour. In the case of oleum, the vapour phase is high in SO_3 .

The above properties of sulphuric acid must be taken into consideration when choosing the operating conditions for the process and when designing pieces of equipment, pipelines, etc. For example, if a sulphuric acid plant is to be installed out-of-doors, a sturdier thermal insulation must be envisag-

ed for the lines carrying sulphuric acid solutions with a sufficiently high crystallization (freezing) point. By referring to the vapour-liquid equilibrium diagram, the designer can choose optimum conditions for the absorption of sulphur trioxide such that a sufficiently high degree of absorption will be achieved and side effects, such as the formation of sulphuric acid mist, will be avoided.

Raw materials and processes for the manufacture of sulphuric acid.

The raw materials for the manufacture of sulphuric acid may be elemental sulphur and sulphur-bearing compounds from which either sulphur or sulphur dioxide can be produced. These compounds are iron sulphides, the sulphides of copper, zinc and other non-ferrous metals, hydrogen sulphide, and some others.

The traditional raw materials for sulphuric acid have always been elemental sulphur and pyrite. In 1980, the Soviet Union manufactured 49% of its sulphuric acid from sulphur and 32% from pyrite. A sizeable contribution (15%) comes from the SO_2 -carrying waste gases of non-ferrous smelteries.

In recent years there has been a growing trend the world over to reclaim sulphur from industrial waste gases as a way of environmental pollution abatement. Fuel-fired power stations and metallurgical plants discharge to the atmosphere far more sulphur than is necessary for the manufacture of sulphuric acid. Taking the year 1980 as an example, the world's consumption of sulphur was 65 million tonnes, and the sulphur lost as SO_2 with waste gases amounted to 100 million tonnes. However, it is not always feasible to reclaim the SO_2 of waste gases because of its low concentration.

Still, waste gases are the cheapest raw material, the wholesale prices of pyrite are likewise low, but elemental sulphur remains a very expensive item. Therefore, for the manufacture of sulphuric acid from sulphur to be economically justified, the industry needs a process in which the cost of sulphur treatment would be materially below that of pyrite or waste gas processing.

Sulphuric acid is manufactured in a number of steps. The first step is to produce sulphur dioxide by the oxidation (roasting) of a sulphur-bearing raw material.* The next step is the conversion of the sulphur dioxide to sulphur trioxide. The reaction involved in this step is associated with a high activation energy, so the use of a catalyst is the rule. There are two distinct processes for the oxidation of SO_2 to SO_3 ; one is called the contact process and the other, the chamber process.

In the *contact process*, SO_2 is oxidized to SO_3 over a solid catalyst. The

* There is no need for this step when waste gases are used as the raw material because sulphide roasting is then a step of some other production process.

sulphur trioxide is converted to sulphuric acid at the last step of the process — the absorption of the sulphur trioxide according to the simple reaction scheme

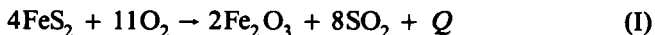


In the *chamber process*, the required oxygen is supplied by nitrogen oxides. The sulphur dioxide is oxidized in a liquid phase, and the end product is sulphuric acid:



At present, commercial sulphuric acid is mainly produced by the contact process as it permits the use of plant items capable of operation at high rates.

The contact process. By this process, the acid can be produced from pyrite or sulphur. The first step in the process is to oxidize the raw material so as to obtain a gas containing sulphur dioxide. Depending on the raw material, one of the following reactions takes place exothermally:



or



In addition to gaseous SO_2 , reaction (I) yields a solid, Fe_2O_3 , which may be present in the gas phase as dust. Pyrite contains various impurities, notably the compounds of arsenic and fluorine, which pass into the gas phase at the roasting step. If they were allowed to be present when the sulphur dioxide is catalytically oxidized to sulphur trioxide, they would poison the catalyst. Therefore, the process gas resulting from the pyrite roasting step must be subjected to a preparatory treatment which, in addition to removal of catalytic poisons, includes removal of water vapour (drying) and recovery of byproducts (compounds of Se and Te).

When the process gas is produced by burning elemental sulphur, there is no need for removal of impurities, and the preparatory treatment will only include drying and heat recovery.

The third step is a reversible exothermic reaction in which the sulphur dioxide is oxidized catalytically to sulphur trioxide:



The final step is the absorption of the sulphur trioxide in concentrated sulphuric acid or oleum.

The various steps in the contact process of sulphuric acid manufacture may be combined in more than one way. Some of the plant designs are illustrated in the flowsheets of Fig. 15.4. One of them is the open-cycle single absorption type of plant.

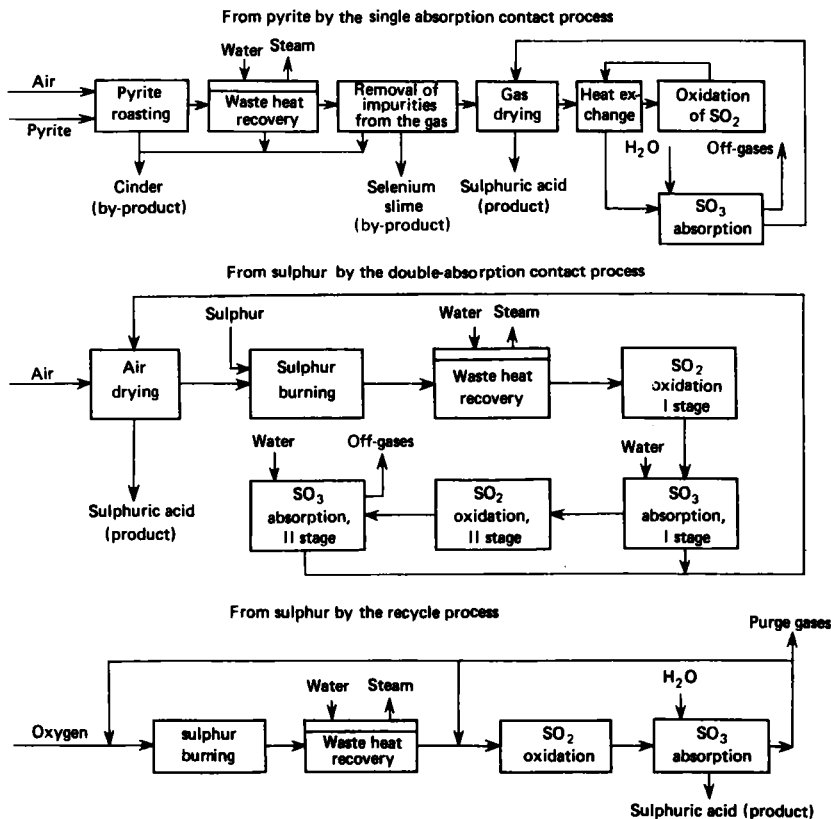


Fig. 15.4 Block diagrams for the manufacture of sulphuric acid

An important consideration in the manufacture of sulphuric acid is to achieve the high conversion of SO_2 to SO_3 . Apart from an increase in acid yield, the high conversion serves to reduce the emission of the objectionable SO_2 to the environment.

The conversion of SO_2 can be enhanced in several ways. Most commonly this is done by using what is known as the double-absorption contact process. Another approach is to use a closed-cycle scheme utilizing technical-grade oxygen.

It is to be noted that the diagrams shown in Fig. 15.4 give only a rough idea about the actual process. Among other things, they do not show the heat transfer between the various streams so important in power cogeneration. Nor do they identify the plant items used, etc. The necessary additional information can be filled in by carrying out physico-chemical and technical analysis of the individual steps.

What follows is a discussion of an open-cycle scheme for the manufacture of sulphuric acid from iron pyrite and sulphur. As follows from the diagrams shown in Fig. 15.4, four major steps may be identified in each case. These are: (1) the production of an SO_2 -carrying gas; (2) preparation of the gas for catalytic oxidation; (3) catalytic oxidation of the sulphur dioxide to sulphur trioxide; (4) absorption of the sulphur trioxide.

Since different plant items will usually be used in each case, there may be some difference between the individual steps, especially as far as step 2 is concerned. The basic approach to their implementation and to the selection of operating conditions as dictated by the objectives to be achieved at each step will however be the same in all of them.

Production of an SO_2 -bearing gas from sulphur. When sulphur is burned, irreversible exothermic reaction (II) takes place with the evolution of a large quantity of heat:

$$\Delta H = -362.4 \text{ kJ mol}^{-1} \text{ or } 362.4/32 = 11.325 \text{ kJ g}^{-1} = 11325 \text{ kJ/kg S}$$

The heat of fusion for sulphur is about 50 kJ kg^{-1} (sulphur melts in the temperature range from 103°C to 119°C , depending on its modification). The heat of evaporation for molten sulphur is 288 kJ kg^{-1} (molten sulphur boils at 444.6°C). Thus, the heat released as sulphur is burned is quite enough both to melt and to vaporize the sulphur, so it will react with oxygen in the gas phase (a homogeneous reaction).

In industrial practice, sulphur is burned in molten state. It can be melted with the steam generated by reclaiming heat from the combustion of sulphur. Since sulphur melts at a relatively low temperature, it is an easy matter to settle and filter it for removal of the mechanical impurities that have failed to pass into the liquid phase, thereby obtaining a feedstock of a sufficiently high purity. Molten sulphur can be burned in two types of sulphur burner, the gun type and the cyclone type. Either type requires that the sulphur be properly atomized for ease of evaporation and for reliable contact with air at any point in the burner.

Figure 15.5 shows a cyclone-type sulphur burner. It consists of a precombustion chamber, 1, and two afterburning chambers, 2 and 3. The burner has an air jacket, 4, which serves to bring down the temperature of the burner shell and to prevent the escape of sulphur dioxide. Two banks of nozzles, 7, force a tangential stream of air, and a mechanical nozzle, 8, supplies a tangential stream of molten sulphur. The gas produced by burning molten sulphur and sulphur vapour are passed via a pinch ring, 6, from the precombustion chamber into the first afterburning chamber, 2, which is also fitted with air nozzles, 9, and a sulphur nozzle, 10. The gas leaves the first afterburning chamber via a second pinch ring, 5, and enters the second afterburning chamber, 3, where the remaining sulphur is burned (some air is added to the gas between the pinch rings). On leaving the

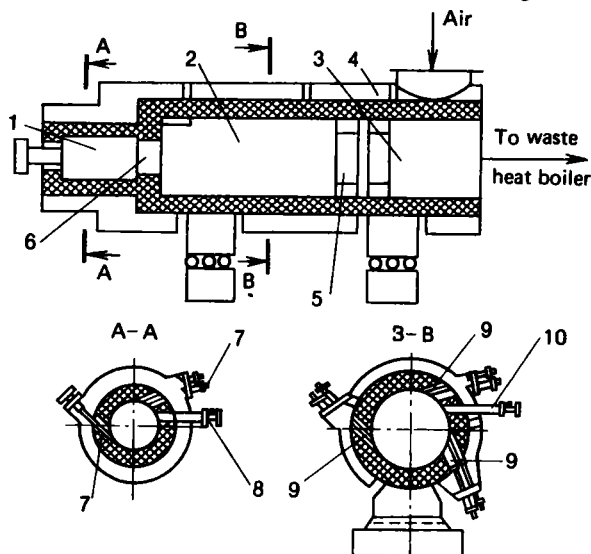


Fig. 15.5 Cyclone sulphur burner:

1, precombustion chamber; 2, afterburning chamber; 3, afterburning chamber; 4, air jacket; 5, pinch ring; 6, pinch ring; 7, air nozzle; 8, sulphur nozzle; 9, air nozzle; 10, sulphur nozzle

sulphur burner, the gas is passed to a waste-heat boiler and to the other vessels downstream.

The SO_2 content of the gas produced by burning sulphur depends on the ratio in which sulphur and air are fed to the burner. If air is taken in a stoichiometric ratio, that is, 1 mole of oxygen per mole of sulphur, complete combustion of the sulphur will produce a gas whose SO_2 content will be equal to the concentration of oxygen in air, that is, $C_{\text{SO}_2, \text{max}} = 21\%$ by volume. Ordinarily, however, air is taken in some excess, since otherwise the temperature in the sulphur burner would have been too high.

When sulphur is burned adiabatically and in a stoichiometric ratio, the temperature of combustion is about 1500°C . Practically, the maximum temperature is limited by the fact that at over 1300°C the lining of the burner and flues rapidly erodes. The gas produced by burning sulphur usually carries 13-14% SO_2 .

Production of the roast gas from iron pyrite. The roasting of iron pyrite might be visualized as proceeding according to the overall reaction of the form of (I) where $Q = 853.8 \text{ kJ per mole of FeS}_2$ or 7117 kJ kg^{-1} . Actually, it proceeds via several intermediate steps. At first, a slow endothermic reaction takes place, causing the thermal decomposition of the iron disulphide. Then follow strongly exothermic reactions in which the sulphur vapour burns and the iron sulphide, FeS , is oxidized.

Some of the atmospheric oxygen is used up to oxidize the iron. Therefore, the maximum attainable concentration of sulphur dioxide in the roast gas is lower than it is when elemental sulphur is burned. It can be determined as follows. In air, for each mole of oxygen there are 79/21 moles of nitrogen and inert gases. If reaction (I) uses the stoichiometric quantity of air, the roast gas will carry $11 \times (79/21) = 41.4$ moles of nitrogen per 8 moles of SO_2 . Hence,

$$C_{\text{SO}_2, \text{max}} = [8/(8 + 41.4)] \times 100 = 16.2 \text{ vol. \%}$$

As a rule, air is taken in excess of its stoichiometric quantity, and the SO_2 content of the roast gas decreases with increasing excess of air. The theoretical concentration of SO_2 in the roast gas (assuming that all of the sulphur present in the iron pyrite is utilized) can be found by the equation

$$C_{\text{SO}_2} = [8/(52.4m - 3)] \times 100 \text{ vol. \%} \quad (15.1)$$

where m is the excess-air coefficient.

Prior to roasting, the iron pyrite is dressed by flotation. In addition to FeS_2 , the flotation pyrite contains some impurities (notably, the compounds of arsenic, selenium, tellurium, and fluorine) which pass into the roast gas as the oxides As_2O_3 , SeO_2 and TeO_2 and the fluorine gases HF and SiF_4 . Because of them, the roast gas needs purification.

The roast gas also contains a small quantity of sulphur trioxide because iron oxide at elevated temperatures catalyzes the oxidation of SO_2 to SO_3 .

Pyrite roasting is a typical heterogeneous process in a gas-solid system which may be described by the unreacted-core model (see Sec. 4.2). With this model, the process involves several diffusion steps and a chemical conversion which likewise occurs in several steps. As a way of increasing the process rate, it is above all sought to minimize the resistance at the diffusion steps, that is, not to effect the roasting operation in the diffusion region. This can be achieved by comminuting the solid phase and by making the flow highly turbulent. This objective can best be achieved with a roaster in which the pyrite charge forms a fluidized bed (the fluidized bed pyrite roaster).

The process temperature must be sufficiently high for the reaction to proceed at a high rate. At low temperatures (below 500°C), the endothermic thermal decomposition of iron disulphide cannot occur at all. On the other hand, when the process temperature is too high, there may occur an objectionable physical process — the burning particles of the charge may sinter together to form larger particles. In consequence, the time to the complete conversion, τ_{comp} , of the solids will be longer and the throughput of the roaster will be reduced. The sintering temperature ranges from 800° to 900°C , depending on the make-up (grade) of iron pyrite. If the roasting

Table 15.1 Comparison of Fluidized-Bed and Multihearth Roasters

Roaster type	Production rate, $\text{kg m}^{-3} \text{d}^{-1}$	SO_2 concentration, vol. %	Dust content, g m^{-3}	Sulphur content of cinder, %
Fluidized-bed	1000	13-15	300	0.5-1
Multiple hearth	200	8-9	10	2

operation were allowed to proceed adiabatically, the temperature would rise too high. To avoid this, some of the roasting heat has to be withdrawn inside the roaster. Most conveniently this can be done in a fluidized-bed roaster because the solid material that makes up the fluidized bed shows a high coefficient of heat transfer from the pyrite to the surface of cooling elements — of the order of $1000 \text{ kJ m}^{-2} \text{hr}^{-1} \text{K}^{-1}$. Also, cooling coils can be laid in the fluidized bed.

Pyrite can generally be roasted in several types of continuous roasters differing in the way the solid phase is moved. Some older sulphuric acid plants are still using mechanical multihearth roasters in which the comminuted material is raked from one hearth to another and burns in the process. There are roasters which handle the charge in pulverized form — the pyrite particles burn as they fall down in a hollow chamber. In cyclone roasters, the pyrite is fed tangentially along with a stream of hot air at a high velocity — the pyrite burns as it is circulated with air inside the roaster, and the molten cinder escapes through the openings provided for the purpose.

At this writing, the most commonly used type of furnace is the fluidized-bed roaster. The fluidized bed provides for a high rate of diffusion and heat-transfer processes (supply of oxygen to the surface of the pyrite grains, withdrawal of the sulphur dioxide into the gas stream, removal of heat from the surface of the bed to the gas stream). Since there is no resistance associated with mass and heat transfer, the roasting operation can be effected at a high rate. Fluidized-bed roasters show the highest rate of operation as compared with any other types. A major drawback of fluidized-bed roasters is the high dust content of the roast gas (Table 15.1).

In sketch form, a fluidized-bed roaster is shown in Fig. 15.6. It is essentially a shaft consisting of a steel shell, 1, lined with a fire-resistant material. At the base of the roaster is a bar screen, 4, with a great number of openings through which the air stream forced from below is uniformly distributed all over the roaster's cross section. The fluidized bed encloses cooling units 5 (mild-steel tubes) joined to the forced circulation system of a waste-heat boiler. Falling through the grate of the discharge chamber, 2, the cinder enters a hopper, 3. The greater proportion (as much as 90%) of

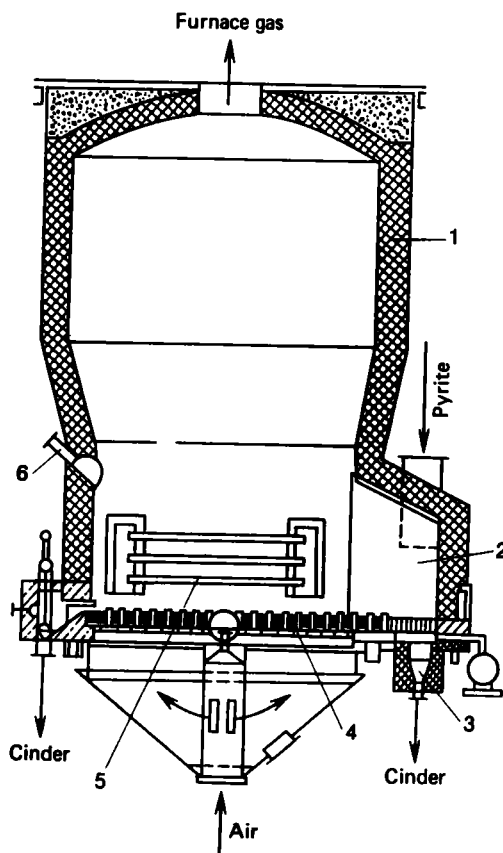


Fig. 15.6 Fluidized-bed pyrite roaster:

1, shell; 2, discharge chamber; 3, cinder hopper; 4, hearth bar screen; 5, cooling units; 6, secondary air duct

the cinder is carried away with the roast gas. The secondary air required for all of the sulphur to be burned is admitted by a duct, 6.

Apart from a pyrite roaster, the roasting section of a plant usually includes a waste-heat boiler and equipment for removal of cinder dust from the roast gas.

Preparation of the roast gas for catalytic oxidation. This step of the process includes removal of the impurities that could cause trouble at the subsequent steps, and also heating (or cooling) to the temperature at which catalytic oxidation can begin.

The gas produced by burning iron pyrite in a fluidized-bed roaster is heavily laden with cinder fines and the compounds of arsenic, selenium,

and fluorine. The purification of the roast gas commences in the roasting section of the plant, where the cinder fines are collected in cyclones and dry electrostatic precipitators. The fines content of the roast gas following dry precipitation ought not to exceed 50 mg m^{-3} . Further cleaning is effected at the wet purification step in the scrubbing section. Thus treated, the roast gas gets rid of the remaining fines, catalyst poisons (compounds of arsenic and fluorine), and compounds of selenium.

Even minute quantities of dust left over from dry purification might lead to an increase in the pressure drop across the plant items and the poisoning of the catalyst by the arsenic compounds adsorbed on the cinder dust. The catalyst might also be poisoned if the gas phase were allowed to retain arsenic oxide and fluorine compounds (HF and SiF_4). Selenium dioxide is not a catalyst poison, but it is a valuable raw material for the manufacture of semiconductors.

The wet scrubbing of the roast gas consists in that it is washed with dilute sulphuric acid. This is accompanied by condensation, absorption, and some other physical operations.

The principal impurities (As_2O_3 , SeO_2 , etc.) present in the roast gas in the gaseous or vapour state are removed with sulphuric acid which has a lower temperature than the gas being scrubbed. Some of these impurities are dissolved in the sulphuric acid, but the greater proportion passes into the sulphuric acid mist. In addition to SO_2 , the roast gas carries small quantities of sulphur trioxide and water vapour — on cooling, they react with each other to form sulphuric acid vapour. In the first scrubbing tower the gas is rapidly cooled, and the sulphuric acid vapour condenses to form the acid mist — fine droplets suspended in the gas.

The overall surface area of the droplets that make up the acid mist is very large, so they dissolve a great quantity of As_2O_3 , SeO_2 and other impurities removed from the gas along with the mist in the scrubbing towers and electrostatic precipitators. Thorough demisting of the roast gas is important not only for removal of its impurities that might poison the catalyst. It is as important to collect the sulphuric acid carried by the mist droplets. As the roast gas is passed through the pieces of equipment and pipelines, the mist could settle on the walls and cause corrosion. When the gas is poorly purified, an especially large amount of acid mist might be deposited in the blowers where the gas stream travels at a high circumferential velocity which favours the separation of fine acid droplets. The effect of the sulphuric acid mist is most detrimental in the converter section. The products of corrosion formed as the sulphuric acid reacts with the metal of the tubes in the converter, preheaters, and heat exchangers are responsible for the increased resistance of the plant units, the reduced heat transfer coefficient, and the formation of a solid crust on the outer layer of the catalyst.

The efficiency of wet scrubbing is enhanced by carrying it out in several pieces of equipment. The first one is a hollow scrubbing tower — the internals of a packed or a tray-type tower would be clogged by the settling dust. The second is a packed scrubbing tower — here the mist droplets coalesce and partly settle out. The remaining mist is collected in wet electrostatic precipitators.

For better removal of acid mist in the electrostatic precipitators, it is practised to bring down the temperature of the gas and the concentration of the spray acid in the second scrubbing tower. Also, the gas emerging from the first electric precipitator is passed through a moistening tower irrigated with a very weak (5%) sulphuric acid. This raises the relative humidity of the gas, the mist droplets absorb water vapour, and their size is increased.

In the second scrubbing and moistening towers the gas is practically fully saturated with water vapour. This might cause acid condensation in the heat exchangers of the converter section and mist formation in the absorber section. As a corollary, a good deal of sulphuric acid might be lost with the off-gases because conventional absorbers show a poor performance in catching the mist. This explains the need for a thorough drying of the roast gas in the gas-cleaning section. The gas is dried in packed towers where the water vapour is absorbed by concentrated sulphuric acid. The moisture content of the gas leaving the drying towers ought not to exceed 0.08 g m^{-3} (0.01% by volume).

The gas produced by burning sulphur is far simpler to prepare for contact oxidation. Sulphur is practically free of the impurities that could become catalyst poisons on burning. Therefore, all that is needed by way of preparation is to dehydrate the gas. Since the dehydration with concentrated sulphuric acid takes place at a low temperature, it is preferable to dehydrate the cold air fed to the sulphur burner rather than the gas as it would have to be cooled. Thus treated, the gas carries a minimal (allowable) quantity of water vapour and needs only to be cooled to the kindling temperature of the catalyst in waste-heat boilers before it enters the converter.

Since no bulky gas-cleaning equipment is needed in the manufacture of sulphuric acid from sulphur, it is said to be manufactured by a short route.

Catalytic oxidation of the sulphur dioxide. This step, reaction (III), involves a very high activation energy, so it can only be effected in the presence of a catalyst.

In industrial practice, the sulphur dioxide is mostly oxidized over a V_2O_5 catalyst. Other materials, above all platinum, also show a sufficient catalytic activity in this reaction. Unfortunately, platinum catalysts are highly sensitive towards even traces of arsenic, selenium, chlorine and

other impurities. This is the reason why the pentavanadium catalyst has all but ousted other catalysts from industrial practice.

Iron (III) oxide, Fe_2O_3 , also shows a catalytic activity, but at high temperatures only. This behaviour of the Fe_2O_3 present in the pyrite cinder may be responsible for the occurrence of minute quantities of sulphur trioxide in the roast gas leaving a fluidized-bed roaster.

The oxidation of sulphur dioxide is a reversible, exothermic reaction. As measured at 500 °C, its enthalpy change is 94.23 kJ mol⁻¹. As a function of temperature, it is described by an equation of the form

$$\Delta H_r = -101\,420 + 9.26\,T \text{ J mol}^{-1}$$

Its equilibrium constant

$$K_p = p_{\text{SO}_3,e} / p_{\text{SO}_2,e} p_{\text{O}_2,e}^{1/2} \quad (15.2)$$

can be found by the equation

$$\log_{10} K_p = (4905.5/T) - 4.6455 \quad (15.3)$$

The equilibrium conversion is

$$x_{\text{SO}_2,e} = (n_{\text{SO}_2,0} - n_{\text{SO}_2,e}) / n_{\text{SO}_2,0} \quad (15.4)$$

According to the reaction stoichiometry, it may be deemed that

$$n_{\text{SO}_2,0} - n_{\text{SO}_2,e} = n_{\text{SO}_3,e}$$

and

$$n_{\text{SO}_2,0} = n_{\text{SO}_2,e} + n_{\text{SO}_3,e}$$

Hence,

$$x_{\text{SO}_2,e} = n_{\text{SO}_3,e} / (n_{\text{SO}_2,e} + n_{\text{SO}_3,e}) \quad (15.5)$$

or, on replacing the equilibrium amounts of the components with their equilibrium partial pressures,

$$x_{\text{SO}_2,e} = p_{\text{SO}_3,e} / (p_{\text{SO}_2,e} + p_{\text{SO}_3,e}) \quad (15.6)$$

On substituting the ratio $p_{\text{SO}_3,e} / p_{\text{SO}_2,e}$ from Eq. (15.2) into Eq. (15.5), we get

$$x_{\text{SO}_2,e} = 1 / (K_p + 1/p_{\text{O}_2,e}^{1/2}) \quad (15.7)$$

On expressing $p_{\text{O}_2,e}$ in terms of the equilibrium conversion (see Sec. 2.4), we have

$$x_{\text{SO}_2,e} = \frac{K_p}{K_p + \left[\frac{100 - ax_{\text{SO}_2,e}}{p(b - 0.5ax_{\text{SO}_2,e})} \right]^{1/2}} \quad (15.8)$$

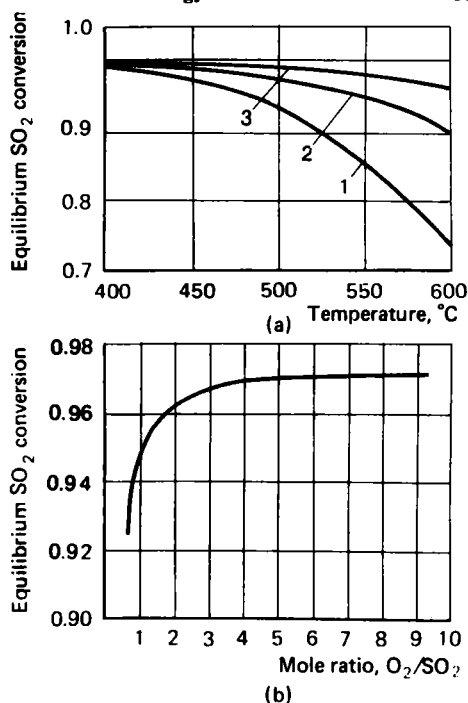


Fig. 15.7 Equilibrium conversion of SO₂ as a function of: (a) temperature at various pressures: 1, 0.1 MPa; 2, 1 MPa; 3, 10 MPa. Feed composition: 7 vol.% SO₂, 11 vol.% O₂, 82 vol.% N₂; (b) molar O₂:SO₂ ratio. Temperature, 475 °C; pressure, 0.1 MPa

where:

- p = total pressure
- a = original SO₂ content of the gas, vol. %
- b = original O₂ content of the gas, vol. %

Equation (15.8) is transcendental with respect to $x_{\text{SO}_2,e}$, so it can only be solved by numerical methods.

The plot in Fig. 15.7a relates the equilibrium conversion $x_{\text{SO}_2,e}$ to temperature at several values of pressure, and the plot in Fig. 15.7b relates the equilibrium conversion of SO₂ to the ratio of the volumetric concentrations of oxygen and sulphur dioxide at constant temperature and pressure.

The reaction rate and the form of the rate equation depend on the type of catalyst used. As already noted, the most commonly used catalyst is pentavalent vanadium. It consists of about 8% by mass V₂O₅ applied to a porous base.*

* This catalyst usually comes in the form of individual pellets or, more commonly, as extruded cylinders. See J.A. Kent, *Industrial Chemistry*, Van Nostrand Reinhold Company, 1974, p. 69 — *Translator's note*.

The catalytic oxidation of sulphur dioxide over a vanadium catalyst proceeds at a rate which is given by

$$\frac{dx_{\text{SO}_2}}{d\tau} = \frac{kp}{a} \frac{1 - x_{\text{SO}_2}}{1 - 0.2x_{\text{SO}_2}} \left[\beta - \frac{x_{\text{SO}_2}^2}{pK_p^2(1 - x_{\text{SO}_2})^2} \right] \quad (15.9)$$

where:

$$\beta = \frac{b - 0.5ax_{\text{SO}_2}}{1 - 0.5ax_{\text{SO}_2}}$$

x_{SO_2} = conversion

τ = contact time

k = rate constant of the forward reaction

a = molar fraction of SO_2 in the feedstock

b = molar fraction of O_2 in the feedstock

K_p = equilibrium constant of reaction (III)

p = pressure

For simplified calculations, use may be made of the Boreskov equation:

$$w_{r,\text{SO}_2} = -dC_{\text{SO}_2}/d\tau = k [(C_{\text{SO}_2} - C_{\text{SO}_2,e})/C_{\text{SO}_3}]^{0.8} C_{\text{O}_2} \quad (15.10)$$

It follows from Eqs. (15.9) and (15.10) that the reaction rate depends on how closely the state of equilibrium is approached, and that it passes through a peak as a function of temperature — as the temperature rises, the rate constant of the forward reaction increases while the equilibrium constant and equilibrium conversion decrease.

Since the reaction rate goes up with increasing oxygen concentration, the industrial process is effected with an excess of oxygen. Taking the manufacture of sulphuric acid from iron pyrite as an example, the gas fed to the converter has the following composition (% by volume): SO_2 , 7-9; O_2 , 9-11; and N_2 , 82. That is, more than three times the stoichiometric quantity of oxygen is taken. For this purpose, the concentrated roast gas (14-15% SO_2) is diluted with air before it enters the converter.

Since the oxidation of SO_2 is an exothermic reaction, it should be effected close to the optimum temperature profile (see Sec. 10.6). Two more constraints are imposed on the choice of operating temperature, related to the properties of the catalyst. The lower temperature limit is the kindling temperature of the vanadium catalyst — it ranges from 400 to 440 °C, depending on the catalyst actually used and the gas composition. The upper temperature limit is 600-650 °C. Above this limit, the catalyst is restructured and loses its activity.

In the temperature range 400-600 °C, it is sought to operate the process so that the temperature falls off with increasing conversion.

Most commonly, industrial converters are of the multistage type with external heat exchange. The heat exchange system is arranged so that most

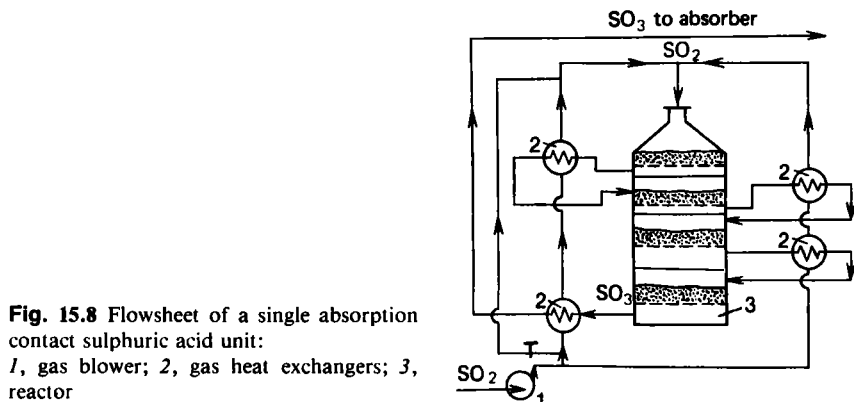


Fig. 15.8 Flowsheet of a single absorption contact sulphuric acid unit:
1, gas blower; 2, gas heat exchangers; 3, reactor

of the reaction heat goes to preheat the feed gas and to cool the gas between the converter stages, as illustrated in Fig. 15.8. The operation of the process close to the optimum temperature profile is illustrated in Fig. 15.9 (line 3).

An important goal for the sulphuric acid industry is to increase the conversion of the sulphur dioxide and to minimize its emissions to the atmosphere. This goal can be achieved in more than one way.

One is a modification of the contact plant which includes two stages of absorption. The rationale of the double-absorption contact process is that

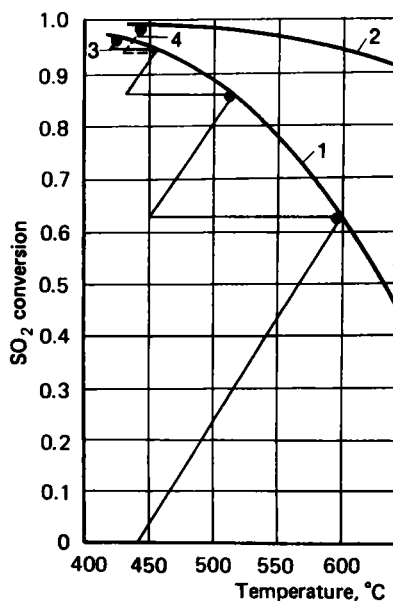


Fig. 15.9 Course of catalytic SO_2 oxidation in a multihearth reactor:
1, equilibrium curve for the feed gas (1st stage in the double-absorption contact process); 2, equilibrium curve for the feed gas after the intermediate SO_3 absorption; 3, last-bed adiabatic curve for the single-absorption contact process; 4, last-bed adiabatic curve for the double-absorption contact process

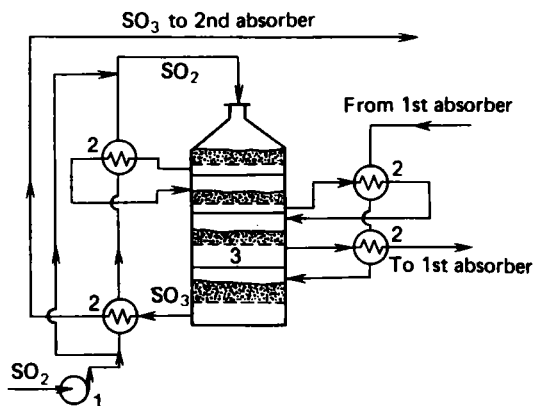


Fig. 15.10 Converter section of a double-absorption contact process sulphuric acid plant:
1, gas blower; 2, gas heat exchangers; 3, converter

the feedstock, in which the SO_2 conversion is 90-95%, is cooled and routed to an intermediate absorber to remove the sulphur trioxide. This markedly raises the oxygen-to-sulphur dioxide ratio in the reaction gas and shifts the reaction equilibrium to the right (equilibrium curve 2 in Fig. 15.9). After re-heating, the reaction gas re-enters the converter where it passes through one or two catalyst beds so that the remaining SO_2 is 95% converted. The overall conversion of SO_2 in the double-absorption contact plant is 99.5-99.8%. The flowsheet of the converter section operating by the double-absorption contact process is shown in Fig. 15.10. As is seen, three catalyst beds are used during the first pass through the converter, and one bed, during the second. The course of the process is illustrated in the plot of Fig. 15.9 (curve 4).

Absorption of the sulphur trioxide. The final step in the manufacture of sulphuric acid by the contact process is the absorption of the sulphur trioxide from the gas mixture and its conversion to sulphuric acid. The absorbent and operating conditions must be chosen so that nearly all of the sulphur trioxide is removed from the gas phase. For this to happen, the partial pressure of SO_3 over the solvent should be negligible because the driving force of absorption will then be very high. On the other hand, one cannot use absorbent solutions over which water vapour would have a high partial pressure. If such a solution were used, the undissolved SO_3 molecules would react with the water molecules in the vapour phase to form sulphuric acid vapour. This vapour would rapidly condense into the sulphuric acid mist consisting of sulphuric acid droplets dispersed in nitrogen:



Since very little of this mist can be caught by conventional absorbers, the

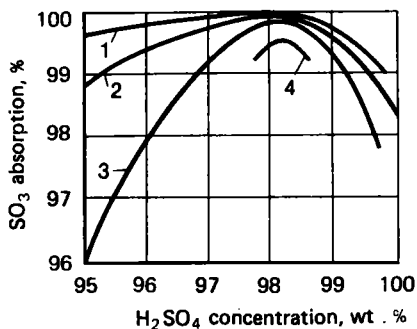
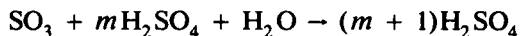


Fig. 15.11 SO₃ absorption in a monohydrate absorber at several temperatures:

1, 60 °C; 2, 80 °C; 3, 100 °C; 4, 120 °C

bulk of it would be carried off by the exit gases to the atmosphere, thus causing air pollution and entailing a further loss of sulphuric acid.

The above reasoning helps to solve the problem of absorbent selection. Referring to the vapour-liquid equilibrium diagram for the H₂O-H₂SO₄-SO₃ system (see Fig. 15.3), it would seem that an optimum absorbent is 98.3% sulphuric acid (technically known as the monohydrate) which has an azeotropic composition. What happens in this case may be described by the following equation:



The use of sulphuric acid of less than 98.3% concentration as the absorbent may, however, lead to the formation of sulphuric acid mist. On the other hand, the partial pressure of SO₃ over 100% sulphuric acid or oleum is very high, so not all of the sulphur trioxide would be absorbed. Still, if one of the products must be oleum, the 1st absorber may well use oleum and the 2nd absorber, 98.3% sulphuric acid.

Ordinarily, the partial pressure of the acid vapour over 98.3% sulphuric acid may be noticeable, and this may reduce the absorption of SO₃ as well. At temperatures below 100 °C, however, the equilibrium pressure of H₂SO₄ vapour is very low, and practically all of the SO₃ may be absorbed (Fig. 15.11).

Thus, to assure a high degree of absorption, the concentration of sulphuric acid in the absorber should be maintained close to 98.3% and the temperature should be kept below 100 °C. As more SO₃ is absorbed, however, the acid gains in strength and, since the reaction is exothermic, its temperature rises, too. To minimize the retarding effect of these factors, the absorption operation is effected so that a single pass through the system raises the concentration of H₂SO₄ by not more than 1-1.5%, the strong sulphuric acid is diluted in a collector to 98.3%, cooled in an external cooler and recycled back to the absorber, thereby maintaining a high recycle ratio.

The flowsheet for the manufacture of sulphuric acid from iron pyrite by the double-absorption contact process. The individual steps we have just examined are combined into a complete plant. The layout of a double-absorption contact plant is shown in the flowsheet of Fig. 15.12.

Referring to the figure, iron pyrite is fed by a weigher to a fluidized-bed roaster, 1. The dust-laden roast gas carrying 13% SO_2 by volume leaves the roaster at a temperature of about 900 °C, goes to a waste-heat boiler 3, and then to cyclone dust collectors 4 and a dry electrostatic dust precipitator for removal of cinder dust. In the waste-heat boiler the roast gas is cooled to a temperature of 420 °C, and the heat thus reclaimed is utilized to raise steam (at a pressure of 4 MPa and a temperature of 450 °C) for power use. The steam may be utilized in the plant itself to drive its compressors and pumps, or elsewhere.

In the scrubbing section consisting of two scrubbing towers, 6 and 7, two pairs of wet electrostatic precipitators 8 and 9, and a drying tower 10, the gas is dewatered and treated for removal of compounds of arsenic, selenium and fluorine. The first scrubber, 6, of the hollow (jet) type operates in the evaporation mode: the circulating acid cools the gas, and the reclaimed heat is used to evaporate the water from the acid supplied to irrigate the tower. The concentration of the spray acid in the first tower is maintained at a constant value of 40-50% by weight H_2SO_4 by diluting it with the 10-15% acid from the second scrubber, 7. The acid withdrawn from the second tower goes to a collector, 18, where it is cooled and returned for irrigation.

Following the second scrubber, the gas is consecutively passed through the two pairs of electrostatic precipitators, 8 and 9, then through the packed drying tower, 10, irrigated with 93-94% sulphuric acid at a temperature of 28-30 °C. The acid circulates between drying tower 10 and collector 18; some of the acid is withdrawn as the product and sent to storage. The concentration of H_2SO_4 in collector 18 is maintained at a constant value by adding 98-99% H_2SO_4 from monohydrate absorbers, 17 and 20. As a way of maintaining a constant temperature at the drying step, the circulating acid is cooled in an air cooler, 22. Before it enters the drying tower, the roast gas is diluted with air so as to bring its SO_2 content down to 9% by volume and to raise the excess of oxygen to a value required for the optimal oxidation of the sulphur dioxide.

On leaving the drying tower, the roast gas is passed through a filter-spray separator, 11, and enters a gas turboblower, 12. In heat exchangers 13, the gas is heated by the heat of reaction to the kindling temperature (420-440 °C) of the catalyst and enters the first bed of catalyst in the converter. In the first catalyst bed, the sulphur dioxide is 74% oxidized and is at the same time raised to 600 °C. On being cooled to 465 °C, the gas is passed through the second catalyst bed where the conversion is raised to

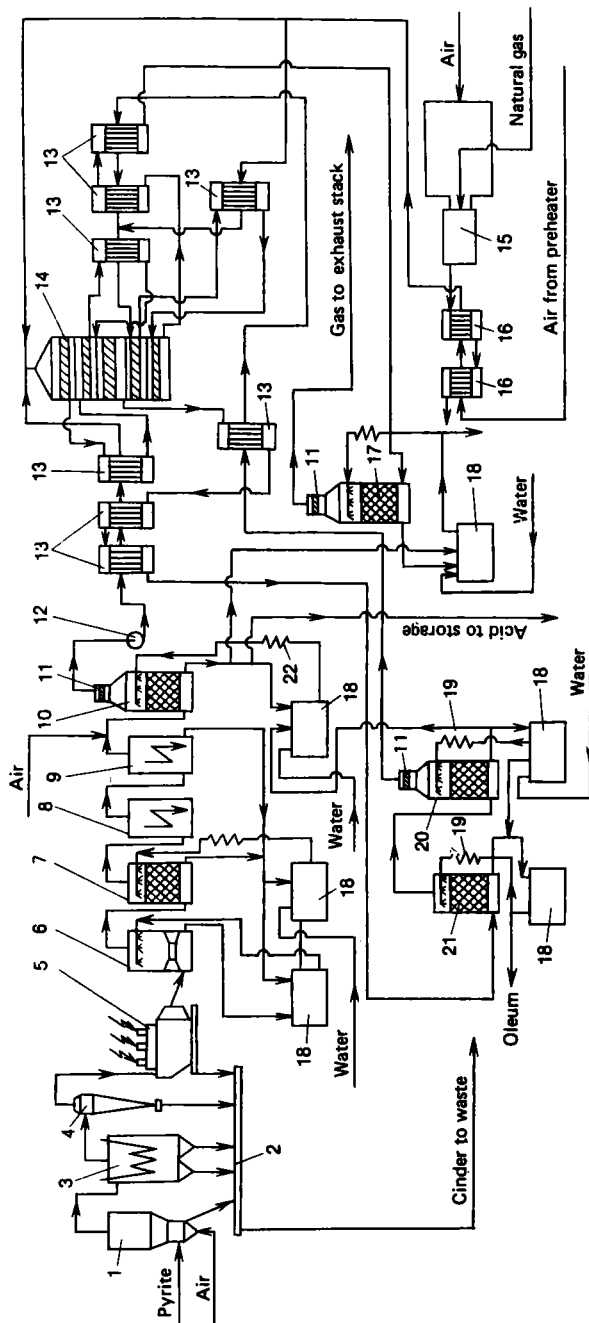


Fig. 15.12 Flowsheet for the manufacture of sulphuric acid by the double-absorption contact process:
 1, roaster; 2, cinder sluicing system; 3, waste-heat boiler; 4, cyclone; 5, dry electrostatic precipitator; 6, jet scrubber; 7, packed scrubber; 8, 9, wet electrostatic precipitators; 10, drying tower; 11, spray separator; 12, gas turbo blower; 13, heat exchangers; 14, converter; 15, start-up preheater; 16, heat exchanger; 17, 2nd monohydrate absorber; 18, acid collectors; 19, coolers; 20, 1st monohydrate absorber; 21, oleum absorber; 22, acid air cooler

86%, and the gas temperature goes up to 514 °C. After it is cooled to 450 °C, the gas is passed through the third catalyst bed where the conversion of the sulphur dioxide rises to 94-94.5%, and the temperature goes up to 470 °C.

Then, as is adopted in the double-absorption contact process, the reaction gas is cooled in heat exchangers 13 to a temperature of 100 °C and routed to the first absorption step: first to the oleum absorber, 21, then to the monohydrate absorber, 20. On passing through the monohydrate absorber and the filter-spray separator, the gas is reheated to 430 °C and passed through the 4th catalyst bed. The SO₂ content of the gas is now 0.75-0.85% by volume. In the 4th catalyst bed, the SO₂ is about 80% oxidized, and the temperature is raised to 449 °C. The reaction mixture is again cooled to 409 °C and passed through the 5th (last) bed of catalyst in the converter. The overall conversion after the five conversion stages is 99.9%. After it is cooled, the gas mixture is routed to the monohydrate absorber, 17, at the second absorption step. The unabsorbed gas consisting mainly of air is passed through a filter, 11, for removal of spray and mist and discharged to the atmosphere via an exhaust stack.

15.2 Fertilizer Technology

Fertilizers are among the most important products of the chemical process industries. The on-going population explosion poses the same problem before all nations in the world — intelligent control of Nature's capacity to reproduce the life-supporting resource, above all food. In tackling this task, fertilizers have long been playing a vital role. Both scientific forecasts and long-term plans envisage a further increase in the world's production of fertilizers at a rate exceeding that of population growth.

Classification of fertilizers. Fertilizers may be classed according to the agronomic role they play in agriculture, their properties, and the manner of manufacture.

From an agronomic point of view, they may be classed into *direct fertilizers* which supply nutrients for plants, and *indirect fertilizers* which enhance soil fertility by improving its physical, chemical and biological properties. Indirect fertilizers include, for example, lime fertilizers which are used to neutralize acid soils, structure-forming fertilizers favouring the aggregation of particles in heavy and clayish soils, etc.

Direct fertilizers may contain one or several nutrients. Accordingly, there are *simple* (or *single-nutrient*) fertilizers and *complex* (or *multi-nutrient*) fertilizers.

A simple fertilizer contains only one of the three principal nutrients nitrogen, phosphorus, or potassium. Quite aptly, there are *nitrogen fertilizers*, *phosphorus fertilizers*, and *potassium* (or *potash*) *fertilizers*.

A complex fertilizer may contain two or three of the principal nutrients. Therefore, there are *double-nutrient fertilizers*, such as NP or PK, and *triple-nutrient fertilizers*, such as NPK. The latter are also called *complete fertilizers*.

A further division of complex fertilizers is into *blended fertilizers* and *compound fertilizers*. A blended fertilizer is a mechanical mixture of constituents which may themselves be single-nutrient or multi-nutrient fertilizers in powder (crystalline) or granulated form. A compound fertilizer is produced by causing the ingredients to react with one another in a reactor to form a compound.

There are elements which are needed to support the plant life in minute quantities. Such elements are called *micronutrients*, and they are introduced into the soil as part of *micronutrient-bearing fertilizers*. Their requirements do not exceed a fraction of a kilogram or a few kilograms per hectare of land. These are salts containing boron, manganese, copper, zinc, and some other elements.

In terms of state of matter, there may be *solid fertilizers*, and *liquid fertilizers* (such as ammonia, aqueous solutions, and suspensions).

The physical properties of fertilizers are a very important factor. Water-soluble fertilizers should be freely flowable and easily drillable. On the other hand, they ought not to be hygroscopic, nor should they cake in storage. On top of that, they must be such that they will be preserved in the soil for a long time and will not be readily washed out by rainwater or blown away by the wind. These requirements are best met by coarse-grained and *granulated fertilizers* whose production has been increasing all the time. Granulated fertilizers can be applied to the soil mechanically, using fertilizer applicators or drills.

Caking in storage can effectively be prevented by treating the granules with surfactants. Recently, there has been a trend towards processes by which the granules are given a coat of some material which prevents caking, on the one hand, and controls the release of the nutrient, on the other. In the latter case, we have *slow-release* or *sustained-action fertilizers*.

Some of the processes used to make phosphorus, nitrogen, and complex fertilizers will be discussed in the pages that follow.

Raw materials for fertilizers. Phosphorus fertilizers are manufactured from apatite and phosphorite (phosphate rock) by converting their phosphorus compounds to forms assimilable by plants.

Nitrogen fertilizers are manufactured from atmospheric nitrogen by converting it to fixed nitrogen, that is, nitrogen compounds. The atmosphere is an inexhaustible source of nitrogen for fertilizers as it contains 78 vol. % N_2 . In fact, it is the sole source of nitrogen for industrial uses because the naturally occurring nitrogen-bearing minerals, such as the salts of nitric acid, are a relatively rare occurrence.

Potassium fertilizers are mainly manufactured from potash rock containing potassium chloride and sulphate.

Apart from naturally occurring raw materials, the fertilizer industry uses some of the subproducts and products of the chemical process and other industries. These are sulphuric, nitric and phosphoric acids and alkalis, above all ammonia which is re-processed into other nitrogen fertilizers and is partly used directly as a liquid fertilizer.

Fertilizers can be recovered from metallurgical slags, the wastes of the food-processing industry, agricultural wastes, and, more recently, domestic wastes.

Manufacture of phosphorus fertilizers. As already noted, the primary sources of raw materials for phosphorus fertilizers are apatite and phosphorite (phosphate rock). The value of the phosphorus compounds thus obtained is based on their P_2O_5 content — total, water-soluble, and citrate-soluble.

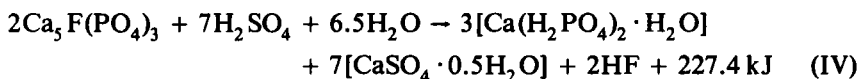
Naturally occurring phosphates may be processed into fertilizers mechanically, thermally, or by acid digestion.

One form of *mechanical processing* is to grind phosphate rock. When applied to an acidic soil, *ground phosphate rock* dissolves in the soil solution very slowly, thus acting as a slow-release fertilizer.

Thermal processing may be based either on the fusion of phosphate rock with silica and alkali salts or on the removal of fluorine by calcination as a means of increasing the availability of P_2O_5 . Thus manufactured, the substances are known collectively as *thermal-phosphate fertilizers*. They include calcined phosphate (such as calcium magnesium phosphate), defluorinated phosphate, fused phosphate, and some others.

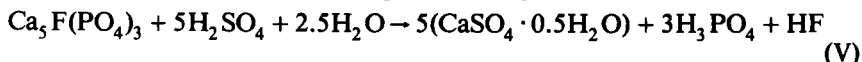
The principal route of phosphorus fertilizer manufacture is, however, *chemical digestion* by causing either sulphuric or phosphoric acid or a mixture of both to react with phosphate rock. When sulphuric acid is used for this purpose, the products are simple (or normal) superphosphate and phosphoric acid which is in turn reprocessed into triple superphosphate, dicalcium phosphate, and compound fertilizers.

Chemistry and technology of normal superphosphate. The process of making normal (or simple) superphosphate consists basically in converting phosphate rock which is insoluble in water and soil solutions to soluble compounds, predominantly monocalcium phosphate, $Ca(H_2PO_4)_2$, with sulphuric acid. This can be described by the following overall reaction scheme:



In practice, the above process proceeds in two steps. During the first step, close on 70% of the apatite reacts with the sulphuric acid to form

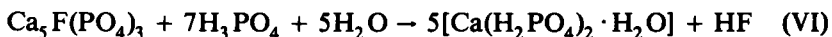
phosphoric acid and calcium sulphate semihydrate:



This step is one of chemical dissolution complicated by the deposition of the calcium sulphate on the phosphate rock grains in the form of a solid or a relatively loose crust. The solid crust strongly retards the diffusion of the liquid phase to the surface of the phosphate, and so the reaction is slowed down; the loose crust does so to a lesser degree. Whether a solid or a loose crust forms depends on the rate of crystallization of the solid phase which is mainly decided by how much the solution is supersaturated with calcium sulphate. In turn, the supersaturation of the solution with calcium sulphate depends on the strength of the sulphuric acid, temperature, and some other factors.

The microscopic crystals of calcium sulphate form a structural lattice which retains a large quantity of the liquid phase, and the superphosphate slurry solidifies. The first step of the acidulation operation (or acid attack) commences immediately after the reactants are mixed together and terminates in a matter of 20-40 min in what are called *dens* (the *denning operation*).

After all of the sulphuric acid has been used up, the second step of the acidulation operation commences, when the remaining apatite (30%) is attacked by the phosphoric acid formed during the first step according to the reaction:



In contrast to calcium sulphate, the monocalcium phosphate does not precipitate at once. It gradually saturates the phosphoric acid solution and begins to crystallize as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ after the solution has been fully saturated. Reaction (VI) proceeds far more slowly than reaction (V), which is explained by the low activity of phosphoric acid and by the crystallization of the solid phases. It commences in the den and continues for 5 to 20 days during the *curing*, or *storage, step* in the pile. After curing in the pile, the fluoroapatite is considered to be fully acidulated, although the superphosphate still carries some undigested phosphate and free phosphoric acid.

In block-diagram form, the manufacture of simple superphosphate is shown in Fig. 15.13. As already mentioned, the process involves three major stages: (1) mixing the rock and acid, (2) reaction in the den to allow the superphosphate slurry to solidify, and (3) curing, or storage, in the pile for a long enough period to permit the conversion to go to completion.

Several measures are usually taken to assure that the reaction of sulphuric acid with phosphate rock, which is a heterogeneous process, will go on at a high rate. These measures are as follows.

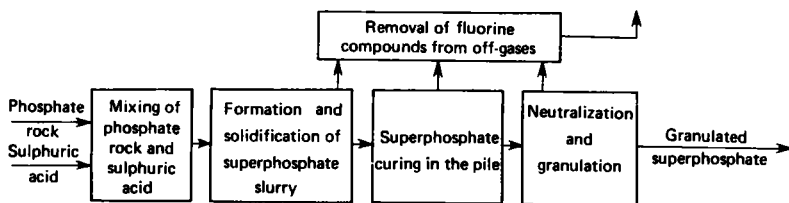


Fig. 15.13 Block diagram of simple superphosphate manufacture

(1) Sulphuric acid for the acidulation of phosphate rock is taken with a small excess (1.07-1.14 times its stoichiometric quantity).

(2) Use is made of 68.5-69.5% sulphuric acid as it is optimal for the calcium sulphate to crystallize. The crystals thus formed are of optimal size for the further digestion of the phosphate.

(3) The temperature in the den is maintained at 115-120 °C as this provides for a sufficiently high rate of acidulation and results in a product (superphosphate) of good physical properties.

After curing in the pile, the superphosphate is upgraded by neutralization with solid agents (limestone, ground phosphorite, etc.), and by granulation.

Figure 15.14 shows a flowsheet for the manufacture of simple granulated superphosphate by a continuous plant incorporating a rotary ring den. Sulphuric acid heated to 55-65 °C is allowed to flow by gravity from a constant-head tank, 4, into an acid mixer, 2, where it is diluted with

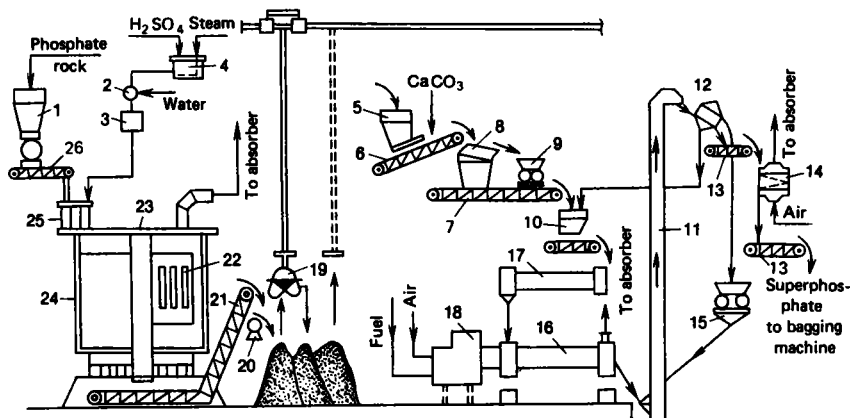


Fig. 15.14 Flowsheet for the manufacture of granulated simple superphosphate:

1, bin; 2, acid mixer; 3, area flowmeter; 4, constant-head tank; 5, den superphosphate bin; 6, conveyor; 7, conveyor; 8, screen; 9, roll mill; 10, neutralized superphosphate bin; 11, elevator; 12, screen; 13, conveyor; 14, cooler; 15, roll crusher; 16, drum drier; 17, drum granulator; 18, combustor; 19, grab bucket; 20, spreader; 21, conveyor; 22, cutter; 23, central (discharge) pipe; 24, den; 25, mixer; 26, weigher

water to obtain 68-68.5% H_2SO_4 . From the mixer, the diluted acid is continuously fed through an area flowmeter, 3, to a mixer, 25, where it is mixed during several minutes with the apatite concentrate coming in from a bin, 1, via a weigher, 26. The mixing operation produces a cream-like thick slurry which continuously enters a den, 24, at a temperature of 110-115 °C. In the den, the sulphuric acid continues to react with the phosphate rock. After the superphosphate slurry solidifies, it is excavated from the den by a cutter, 22. The excavated superphosphate is discharged through the central (discharge) pipe, 23, from the den and transferred by a belt conveyer, 21, for storage in the pile. As it falls down from the conveyer, the superphosphate lands on a spreader, 20, which breaks up the superphosphate lumps. As this is done, some of the moisture is evaporated and the superphosphate is cooled.

The fluorine-carrying off-gases from the den are transferred for fluorine removal to absorption chambers irrigated with water or dilute hydrofluosilicic acid. In operation with a recycle, a 8-10% solution of H_2SiF_6 is accumulated in the absorbers. This solution is likewise withdrawn for re-processing.

The superphosphate is cured for 5 to 20 days in piles 6 to 10 m high. In the meantime, it is re-shoveled two or three times with a grab bucket, 19, for better cooling.

The cured superphosphate is mixed with dry limestone for neutralization, classified on a screen, 8, to remove the oversize, and ground in a roll mill, 9. Following that, the powdered superphosphate is mixed in a drum granulator, 17, with the recycle,* moistened, and rolled into granules as the drum rotates.

Wet (or "green") granules are dried in a drum drier, 16, with flue gases. The dried product is classified on a vibrating screen, 12. The granules 1-4 mm in size make up the product. It is cooled with air in a fluidized-bed cooler, 14, and sent to a bagging machine. The undersize is returned to granulation, and the oversize is ground in a crusher, 15, and returned by an elevator, 11, to the screen for re-classification.

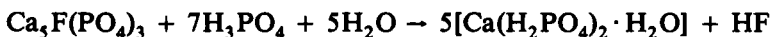
Simple granulated superphosphate is a cheap phosphorus fertilizer. It suffers, however, from a serious shortcoming — it is low in the primary component (19-21% available P_2O_5) and has a sizeable proportion of the objectionable calcium sulphate. As a rule, it is manufactured close to fertilizer users because it is more attractive economically to carry the phosphate rock concentrate to superphosphate plants than the low-grade simple superphosphate to distant users.

* Here the term 'recycle' refers to the off-size fraction of the product, both the undersize or the oversize, which is returned to the process after screening.

A more valuable phosphate fertilizer can be manufactured on replacing sulphuric acid for the acidulation step with phosphoric acid. In fact, this is the basis of triple superphosphate manufacture.

Chemistry and technology of triple superphosphate. Triple superphosphate* is a concentrated phosphate fertilizer produced by digesting phosphate rock with phosphoric acid. It analyzes 42-50% available P_2O_5 , including 27-42% water-soluble P_2O_5 , which is 2 or 3 times the amount present in simple superphosphate. In appearance and phase composition, triple superphosphate is similar to normal superphosphate, but it is nearly free from the ballast, calcium sulphate.

When phosphate rock is digested with phosphoric acid, reaction (VI) takes place, similar to that occurring during the second step in the manufacture of normal superphosphate:



The phosphoric acid required for the above reaction is produced from the same raw material, phosphate rock. This can be done by what is known as the *wet process*: the rock is acidulated with concentrated sulphuric acid; or by the *dry (electric-furnace or, simply, furnace) process*: the phosphate is reduced to phosphorus at a very high temperature, volatilized, then oxidized, and hydrolyzed to phosphoric acid of high purity.

Triple superphosphate may be manufactured following the same route as in the case of simple superphosphate. This is the *den process* of triple superphosphate manufacture. Among its shortcomings are prolonged curing in the pile, accompanied by uncontrolled emissions of objectionable fluorine compounds into the atmosphere, and the need to use concentrated phosphoric acid.

A more advanced form is a *slurry-granulation process*** which uses the less expensive unevaporated phosphoric acid, runs continuously, and needs no prolonged bulk storage in the pile.

The flowsheet for the manufacture of granulated triple superphosphate by the continuous slurry-granulation process from ground phosphate rock and unevaporated wet-process phosphoric acid is shown in Fig. 15.15.

Referring to the figure, ground phosphate rock and phosphoric acid are fed to acidulation tanks, 4. In about an hour, the acid digests 55-60% of the rock at a temperature of 70-90 °C. The slurry leaving the tanks is divided into two streams. One stream (about half the total) is dried by flue gases

* The product has also been known as double, or concentrated, superphosphate, but these terms have largely fallen out of use. — *Translator's note.*

** One example, used outside the USSR, is the Dorr-Oliver granular process. See Sauchelli "Chemistry and Technology of Fertilizers". Reinhold Publishing Corp., 1960 — *Translator's note.*

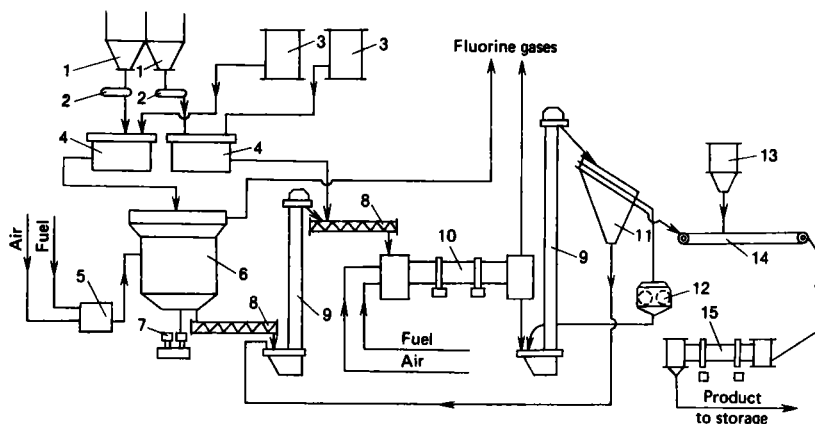


Fig. 15.15 Flowsheet for the manufacture of triple superphosphate from ground phosphate rock and unevaporated wet-process phosphoric acid by the continuous slurry-granulation process:

1, ground phosphate rock bin; 2, weigher; 3, phosphoric acid pressure tank; 4, acidulation tank; 5, furnace; 6, spray drier; 7, rake drive; 8, blunger; 9, elevator; 10, drum drier; 11, screen; 12, crusher; 13, milled chalk bin; 14, belt conveyor; 15, drum neutralizer

in a spray-type drier. The dried fine-grained material is granulated. To this end, it is mixed with the second stream of slurry in a blunger, 8, which also receives a small quantity of recycle. The 'green' granules leaving the blunger carry 20-22% moisture and are therefore dried in a concurrent-flow rotary drier to a moisture content of 3-4%.

As the drying operation is carried out, the acidulation of the feed goes on, and the overall conversion is raised to 80-90%.

The product leaving the rotary drier is passed to a screen. The granules measuring 1-4 mm across are neutralized with chalk in a crusher, mixed with the fines (under 1 mm in size), and recycled to the blunger.*

Normal and triple superphosphate contains P_2O_5 in a form readily assimilable by plant life. In recent years, however, there has been growing interest in controlled-release fertilizers, notably those of the prolonged-action type. This effect can be assured by giving superphosphate granules a coat of material which controls the release of the nutrients from the fertilizer granules. As an alternative, triple superphosphate is mixed with ground phosphate rock. Recently, a sustained-action phosphate fertilizer, sold by the trade name of *Superphos*, has been developed in the USSR. It analyzes 37-38% P_2O_5 of which amount nearly

* Since the material is recycled many times, small particles become coated with successive layers of slurry and grow in size to form hard, round granules. See Sanchelli, op. cit., p. 187 — *Translator's note.*

half is in a quick-release, water-soluble form, and the remainder in a slow-release form. This fertilizer produces a lasting effect on the soil.

Nitrophosphate processes. Compound fertilizers. It is promising to make fertilizers by the direct action of nitric acid on phosphate rock. This route has the advantage of yielding a fertilizer containing both nitrogen and phosphorus as nutrients and of using nitric acid instead of sulphuric acid to convert the insoluble neutral phosphates to a soluble form. Nitrophosphate processes provide the basis for the manufacture of NP or NPK compound fertilizers.

The principal reaction of the processes is



Reaction (VII) yields an *acidulation* or *nitrophosphate slurry* which contains calcium nitrate and free phosphoric acid. This slurry may further be processed in more than one way. In many cases, it is neutralized with ammonia, and this gives ammonium phosphate, an NP fertilizer. If potassium salts (KCl or K_2SO_4) are added to the slurry prior to granulation, the result will be a triple-nutrient, or NPK, fertilizer, such as Nitroammophoska.

In many nitrophosphate processes, the calcium phosphate $\text{Ca}(\text{NO}_3)_2$ which results from Reaction (VII) is removed from the slurry by freezing-out. This route provides for the recovery of all values present in the raw material and a practically wasteless processing because there are no wastes to dispose of, including phosphogypsum. Apart from the manufacture of NPK fertilizers, the nitrophosphate processes can yield other valuable materials, such as strontium, rare-earth elements, etc., in demand in various industries (electronics, metallurgy, etc.).

A generalized block diagram illustrating a nitrophosphate process yielding an NPK fertilizer and the co-products rare-earth oxides, calcium fluoride, and ammonium nitrate, is shown in Fig. 15.16.

Manufacture of nitrogen fertilizers. This is an important class of fertilizers which include ammonium nitrate, urea, ammonium sulphate, aqueous solutions of various nitrates, etc. Nitrogen plays an extremely important role in plant life — it is part of chlorophyll which is the receptor of solar energy, and of protein which is building material for the living cell. Plants can assimilate only fixed nitrogen in the form of nitrates, ammonium salts or amides. A relatively small quantity of fixed nitrogen is produced by soil microorganisms. However, present-day intensive farming can no longer exist without the additional supply of nitrogen in the form of industrially produced nitrogen fertilizers.

Nitrogen fertilizers differ in their nitrogen content, the form of nitrogen compounds (nitrate, ammonia, and amide fertilizers), and state of

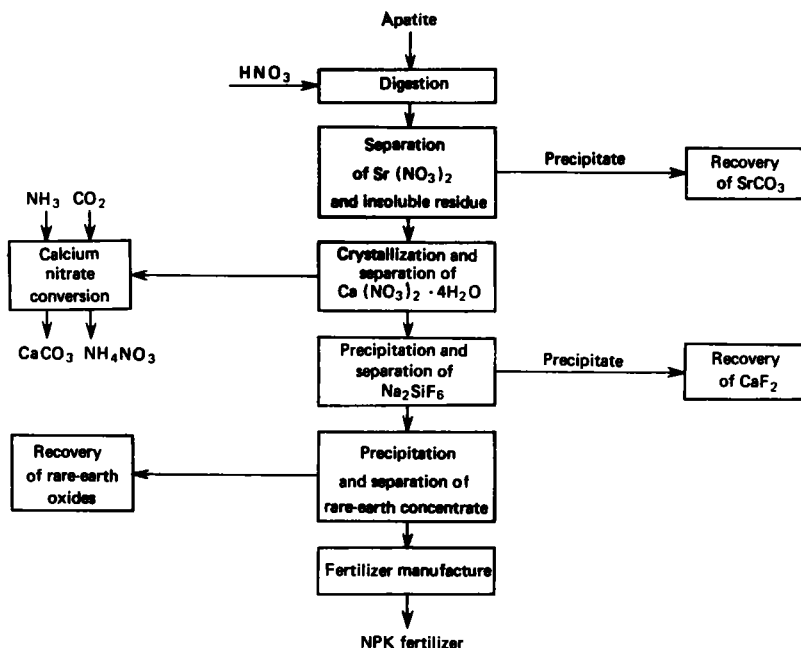


Fig. 15.16 Block diagram for the manufacture of ammonium phosphate-nitrate by the nitric acid attack of phosphate rock

matter (solid and liquid fertilizers). There are also physiologically acidic and physiologically basic fertilizers.

Manufacture of ammonium nitrate. Ammonium nitrate, NH_4NO_3 , is a white, crystalline material which analyses 36% nitrogen in ammoniate and nitrate forms. Both of these forms are readily assimilable by plant life. It is used in large quantities prior to sowing and in all forms of dressing. On a smaller scale, ammonium nitrate is used in the manufacture of explosives.

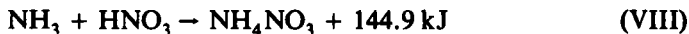
Ammonium nitrate is highly soluble in water and highly hygroscopic. Because of this, the fertilizer loses its crystalline form and cakes into a solid, monolithic mass.

Several processes exist to make a non-caking form of ammonium nitrate. One is *prilling**. The overall surface area of prills, which are uniform rounded grains or pellets, is smaller than that of an equal amount of the powdered fertilizer. This is the reason why prilled or otherwise granulated fertilizers absorb moisture from the atmosphere less eagerly. Sometimes ammonium nitrate is fused with less hygroscopic salts, such as

* Other processes are the Stengel process, crystallization and graining. See V. Sauchelli, Op. cit., p. 26. — *Translator's note.*

ammonium sulphate. The same purpose can be served by ammonium phosphate, potassium chloride, and magnesium nitrate.

The basis of ammonium nitrate production is the homogeneous reaction between gaseous ammonia (ammonia vapour) and dilute nitric acid:



The reaction proceeds at a high rate; in an industrial-scale reactor it is limited by the dissolution of the gas in the liquid. It is important to agitate the reactants vigorously so as to minimize the retarding effect of diffusion.

A high process rate can be provided for to a marked extent in the design of the reactor. One example is the heat-of-reaction neutralizer (Fig. 15.17) in which Reaction (VIII) goes on non-stop. The reactor is a vertical vessel consisting of a reaction zone and a separation zone. The reaction zone includes a reaction cylinder, 1, which has openings at its base for the circulating stream. Located somewhat above the openings is a sparger, 2, to feed the ammonia vapour, and still higher up another sparger, 3, to feed nitric acid. The vapour-liquid reaction mixture leaves the reaction cylinder

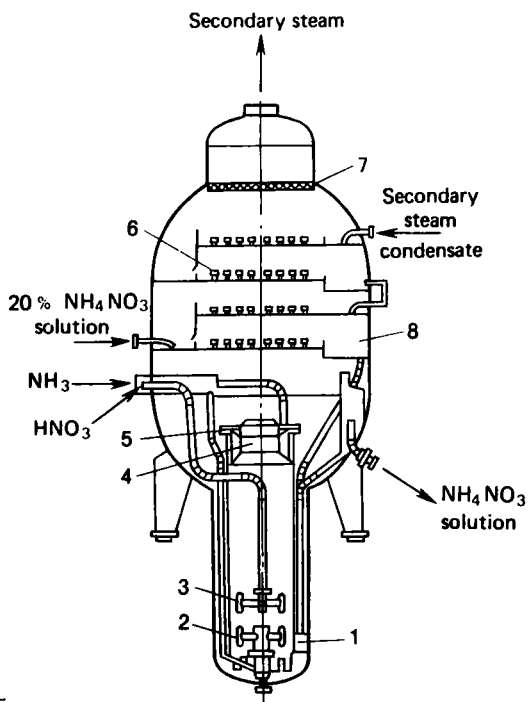


Fig. 15.17 Heat-of-reaction neutralizer:

1, reaction cylinder; 2, ammonia sparger; 3, nitric acid sparger; 4, diffuser; 5, whirler; 6, bubble-cap trays; 7, spray baffle; 8, scrubber

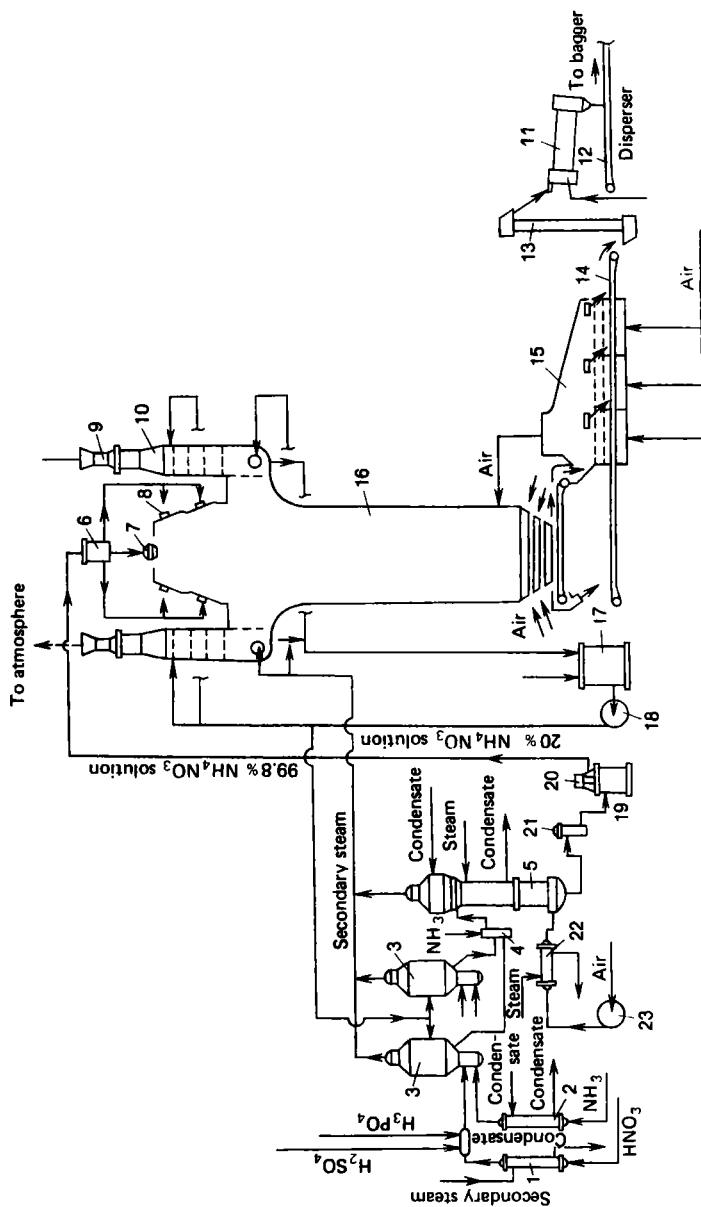


Fig. 15.18 Flowsheet of the ammonium nitrate unit:

1, acid preheater; 2, ammonia preheater; 3, heat-of-reaction neutralizer; 4, post-neutralizer; 5, evaporator; 6, constant-head tank; 7, 8, prilling headers; 9, fan; 10, scrubber; 11, drum; 12, conveyor; 13, elevator; 14, conveyer; 15, fluidized-bed cooler; 16, prilling tower; 17, collector; 18, pump; 19, melt tank; 20, pump; 21, melt filter; 22, air preheater; 23, fan

at the top. Some of the liquor goes from the reactor to a post-neutralizer, and the remainder (the circulating stream) flows downwards. The secondary steam evolved from the liquor is washed free of ammonia nitrate liquor droplets and nitric acid vapour with a 20% solution of ammonium nitrate and then with the secondary-steam condensate on bubble-cap trays, 6.

The heat released by Reaction (VIII) is partly utilized to vaporize water from the liquor. The difference in temperature between the various points in the reactor adds to the agitation of the liquor.

In addition to the neutralization of nitric acid with ammonia, the manufacture of ammonium nitrate also includes the evaporation of the ammonium nitrate liquor, spraying of the molten ammonium nitrate into prills, cooling of the prills, treatment of the prills with surfactants, packaging, storage, loading, and purification of gas emissions and effluents.

The process flowsheet of a state-of-the-art 1360 t/d ammonium nitrate plant is shown in Fig. 15.18. In this tonnage plant, 58-60% nitric acid is raised to 70-80 °C in a preheater, 1, with secondary (liquor) steam from a heat-of-reaction neutralizer, 3, and goes to the neutralization step. Before it enters the neutralizer, phosphoric and sulphuric acids are added in amounts such that the product will analyze 0.3-0.5 P₂O₅ and 0.05-0.2% ammonium sulphate.

The plant includes two neutralizers operating in parallel. In addition to nitric acid, they also receive ammonia vapour heated in a preheater, 2, with steam condensate to 120-130 °C. The quantities of nitric acid and ammonia vapour are controlled in such a way that the liquor leaving the neutralizer has a small excess of nitric acid (2-5 g l⁻¹) to assure a complete absorption of the ammonia.

At the base of the neutralizer, the acids are neutralized at a temperature of 155-170 °C; this produces a concentrated liquor carrying 91-92% NH₄NO₃. At the top of the neutralizer, the secondary (or liquor) steam is washed free of ammonium nitrate droplets and nitric acid vapour. The heat of the secondary steam is partly used to preheat the nitric acid. Following that, the secondary steam is purified and discharged to the atmosphere.

The ammonium nitrate liquor still carrying some nitric acid goes to a post-neutralizer, 4, which also receives the ammonia required to neutralize the remaining free nitric acid. Next, the liquor is fed to an evaporator, 5. The resulting melt carrying 99.7-99.8% ammonium nitrate at 175 °C is passed through a filter, 21, and transferred by a submersible centrifugal pump, 20, to a constant-head tank, 6, and then to a rectangular metal prilling tower, 16.

At the top of the prilling tower are located two prilling headers or spray formers, 7 and 8, which spray the incoming concentrated ammonium nitrate solution, or melt, down inside the tower which receives a stream of

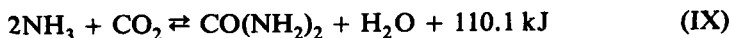
air to cool the falling droplets of ammonium nitrate. During the fall from a height of 50-55 m the droplets cool and harden to solid spherical pellets called prills. As they leave the tower, the prills have a temperature of 90-110 °C. Therefore, they are cooled in a fluidized-bed cooler, 15, which is a rectangular tank divided into three sections and fitted with a perforated grate. Blowers feed air beneath the grate, thus setting up a fluidized bed of prills transferred from the prilling tower by a conveyer. On cooling, the air goes to the prilling tower.

The ammonium nitrate prills are transported by a conveyer, 14, to a coating drum, 11, where they are given a coat of surfactants. The finished fertilizer is then carried by another conveyer, 12, to a bagging machine.

The air leaving the prilling tower is polluted with ammonia nitrate particles, and the secondary steam from the neutralizer and the vapour-air mixture from the evaporator contain unreacted ammonia and nitric acid and also entrained ammonium nitrate particles. These streams are purified at the top of the prilling tower by six parallel-operating tray-type scrubbers, 10, sprayed with a 20-30% solution of ammonium nitrate transferred by a pump, 18, from a collector, 17. Some of this solution is routed to the neutralizer to scrub the secondary steam and is then added to the ammonium nitrate liquor, thus contributing to the product. The purified air is exhausted from the granulator by a fan, 9, and discharged to the atmosphere.

Urea manufacture. Among the nitrogen fertilizers, urea ranks second after ammonium nitrate in terms of production. Its production has been growing thanks to the many uses that it has found in agriculture. It is less susceptible to leaching out as compared with other nitrogen fertilizers, that is, lesser amounts of urea can be washed out of the soil; it is less hygroscopic, and may be used not only as a fertilizer, but as a supplement to animal feeds. Also, urea is widely used to make blended and compound fertilizers, controlled-release fertilizers, plastics, cements, varnishes and other protective coatings.

Urea, $\text{CO}(\text{NH}_2)_2$, when chemically pure, is a colourless, crystalline material analyzing 46.6% nitrogen by weight. Its production is based on the reaction of ammonia with carbon dioxide:

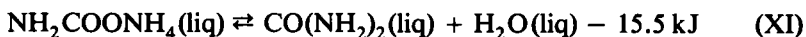


Thus, the raw materials for urea are ammonia and carbon dioxide emerging as a by-product in the manufacture of ammonia synthesis gas. This is the reason why urea manufacture is usually combined with ammonia manufacture at chemical plants.

Reaction (IX) is an overall reaction. Actually, it occurs in two stages. During the first stage, ammonium carbamate is synthesized according to the scheme:



During the second stage, the water is endothermally split off the carbamate molecules to form urea:



The formation of ammonium carbamate is a reversible, exothermic reaction which proceeds with a reduction in volume. In order to shift the equilibrium towards the product, the reaction must be effected at an elevated pressure. Also, for the reaction rate to be sufficiently high, an elevated temperature is required. The rise in pressure counteracts the shift in equilibrium to the left caused by the elevated temperature. In practice, urea is synthesized at a temperature of 150-190 °C and a pressure of 15-20 MPa. In these conditions, the reaction proceeds at a high rate and practically to completion.

The decomposition of ammonium carbamate is a reversible, endothermic reaction proceeding at a high rate in the liquid phase. The reaction should be effected at a temperature not below 98 °C (which is the eutectic point for the $\text{CO}(\text{NH}_2)_2$ - $\text{NH}_2\text{COONH}_4$ system) so as to prevent the crystallization of solids in the reactor. A temperature higher than that will shift the reaction equilibrium to the right and step up its rate. The maximum conversion of the carbamate to urea is achieved at 220 °C. The equilibrium of this reaction can also be shifted by adding an excess of ammonia which, on tying up the reaction water, removes it from the reaction zone. Yet, a complete conversion to urea cannot be achieved. Apart from urea and water, the reaction mixture also contains ammonia carbamate, ammonia, and CO_2 .

If all of the feedstock is to be utilized, provision should be made either for recycling the unreacted ammonia and carbon dioxide along with the intermediates (carbon-ammonium salts) to the synthesis reactor, generally called the reaction autoclave, as is done in processes with a recycle, or for the separation of the urea from the feedstock, with the remaining reactants sent to other processes, such as the manufacture of ammonium nitrate, as is done in processes without a recycle, also known as 'one-pass' or 'once-through' synthesis.

In 'one-pass' synthesis, the melt leaving the autoclave is expanded to atmospheric pressure so that the equilibrium of Reaction (X) at 140-150 °C is shifted practically fully to the left and all of the remaining ammonium carbamate is decomposed. The liquid phase only retains an aqueous solution of urea, which is evaporated and sent to the prilling step. The recycling of the resultant ammonia vapour and carbon dioxide would have required their compression to the pressure of urea synthesis. Also, technical difficulties could have arisen due to the likely formation of ammonia carbamate at low temperature and high pressure already in the compressor and the consequent plugging of the vessels and pipelines with solids.

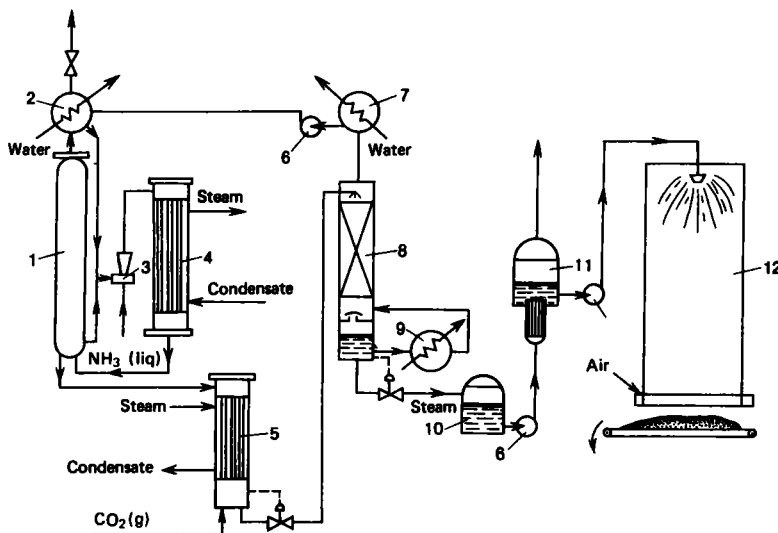


Fig. 15.19 Simplified flowsheet for the manufacture of urea (complete liquid recycle and stripping):

1, urea reaction autoclave; 2, high-pressure scrubber; 3, injector; 4, high-pressure carbamate condenser; 5, stripper; 6, pumps; 7, low-pressure condenser; 8, low-pressure rectifying column; 9, preheater; 10, collector; 11, evaporator; 12, prilling tower

In most cases, therefore, urea processes use what is known as solution, or liquid, recycle. There are several variants of this route. Those leading the field are the complete solution recycle schemes and the stripping processes. The stripping operation consists in that the ammonium carbamate which leaves the reaction autoclave as a melt is caused to decompose at a pressure close to that maintained at the synthesis step, and the melt is blown with compressed CO₂ or compressed ammonia. In these conditions, the ammonium carbamate decomposes because when compressed CO₂ is blown through the melt, the partial pressure of the ammonia is abruptly brought down, and the equilibrium of Reaction (X) is shifted to the left. The stripping processes utilize the heat of ammonium carbamate formation and therefore require less energy.

A simplified flowsheet of a tonnage urea synthesis plant using a solution (liquid) recycle and stripping is shown in Fig. 15.19. As is seen, the plant may be divided into a high-pressure unit, a low-pressure unit, and a prilling system. The aqueous solution of ammonium carbamate along with carbon-ammonium salts, ammonia, and carbon dioxide leave a high-pressure condenser, 4, and enter the base of an urea reaction autoclave, 1. In the autoclave, the formation of ammonium carbamate is carried to completion at a temperature of 170-190 °C and a pressure of 13-15 MPa, and

urea is synthesized. The flow rate of the reactants is adjusted so that the molar $\text{NH}_3:\text{CO}_2$ ratio in the autoclave is 2.8:1 or 2.9:1. The melt leaving the autoclave enters a stripper, 5, where it flows down the tubes, counter-current to a stream of carbon dioxide compressed to 13-15 MPa and mixed with air so that the oxygen content of the mixture is 0.5-0.8% by volume. Air is added to the carbon dioxide in order to promote the formation of a passivating film and to minimize the corrosion of the equipment. The stripper is heated with steam. Leaving the stripper, the vapour-gas mixture carrying fresh carbon dioxide enters the high-pressure condenser which also receives liquid ammonia serving as the working fluid in the injector, 3, that feeds the solution of carbon-ammonium salts to the condenser from a high-pressure scrubber, 2, and also, when necessary, some of the melt from the urea reaction autoclave. As a result, ammonia carbamate is formed in the condenser. The heat of reaction may be used to raise steam.

The unreacted gas continuously emerging from the top of the urea autoclave is conveyed to the high-pressure scrubber where most of the gas is condensed due to water cooling and forms an aqueous solution of ammonium carbamate and carbon-ammonium salts.

The aqueous solution of urea leaving the stripper carries 4-5% ammonium carbamate. For its final decomposition, the solution is expanded to a pressure of 0.3-0.6 MPa and conveyed to the top of a rectifying column, 8. The liquid phase flows down the packing countercurrent to the vapour-gas mixture rising upwards. Leaving the autoclave at the top are NH_3 , CO_2 , and water vapour. The water vapour is condensed in a low-pressure condenser, 7, and dissolves the greater proportion of the ammonia and carbon dioxide. The liquor thus produced is passed to the high-pressure scrubber. Before they are discharged to the atmosphere, the off-gases are finally purified by absorption (not shown in the flowsheet).

The 70% aqueous solution of urea leaving the base of the rectifying column is separated from the vapour-gas mixture and sent, after its pressure has been brought down to atmospheric, for evaporation and prilling. Before it is sprayed into droplets in the prilling tower 12, the melt is mixed with conditioning agents, such as urea-formaldehyde resin, so that the finished fertilizer will not cake or otherwise degrade in storage.

15.3 Environmental Pollution Abatement in the Manufacture of Sulphuric Acid and Fertilizers

As sulphuric acid and fertilizer plants increase in unit capacity, there is a growing risk of environmental pollution even though the concentration of objectionable substances in plant emissions may be relatively low. Therefore, the prevailing trend in these industries is to set up closed-cycle production schemes with no or very little wastes and to minimize the

discharge of objectionable substances to the atmosphere and to water bodies and courses.

In the manufacture of sulphuric acid, better utilization of sulphur dioxide is assured by the double-absorption contact process. It is also possible to employ high-pressure and cyclic schemes.

Existing sulphuric acid plants pollute the biosphere with sulphur dioxide and trioxide; the wash waters from the scrubbing step also carry toxic substances such as arsenic compounds. Where plants operate at a low conversion (98% or less), the emission of sulphur dioxide can be reduced by subjecting the waste gases to sanitary purification. This can be done by absorption methods, such as the sulphite-bisulphite process based on the reaction of SO_2 with aqueous solutions of ammonium sulphite. Sulphur trioxide and, especially, sulphuric acid mist can be removed by passing the off-gases through demisters, gas catchers and suitable filters. Where necessary, electrostatic precipitators may be installed at the exhaust from the sulphuric acid system. Wastewaters from the manufacture of sulphuric acid must be thoroughly purified to remove arsenic compounds.

The manufacture of phosphorus fertilizers is a source of the potential risk of polluting the atmosphere with fluorine-bearing gases. Recovery of fluorine compounds is important not only from the view-point of environmental pollution abatement — fluorine is a valuable raw material for Freons, fluoroplastics, fluorinated rubber, and other materials. Fluorine-bearing gases are absorbed in water with the formation of fluosilicic acid. Fluorine compounds may find their way into sewers from fertilizer scrubbing and gas purification steps. One way to cut down the quantity of these effluents is to use water recirculation systems. Wastewaters can be treated for removal of fluorine compounds with ion exchangers, iron and aluminium hydroxides, aluminium oxide, etc.

Wastewaters from the manufacture of nitrogen fertilizers carry ammonium nitrate and urea. Before they are sent for biological purification, they are mixed with other wastewaters in a ratio such that the concentration of urea is not over 700 mg l^{-1} , and that of ammonia, $65\text{--}70 \text{ mg l}^{-1}$.

An important operation in the manufacture of fertilizers is removal of dust from off-gases. The risk of air pollution with fertilizer dust is especially great at the prilling step. Therefore, the off-gas from priller towers must be subjected to purification by both dry and wet methods.

Chapter Sixteen

PETROLEUM TECHNOLOGY

Sizeable quantities of 'crude oil', as petroleum when just obtained from the ground and before refined in any way is called, were produced for the first time in 1880. Since then its production has been expanding exponentially. At this writing, the world's annual production of crude oil is estimated at $3.2 \times 10^9 \text{ m}^3$.

Crude oil is a mixture of many hundreds of compounds. The principal compounds are the hydrocarbons alkanes, cycloalkanes, and arenes. The alkanes (saturated hydrocarbons) account for 50-70% of the total. The cycloalkanes, mostly monocyclic, may run as high as 30-60% of the total. The most common among them are cyclopentane and cyclohexane. The alkenes (unsaturated hydrocarbons) are not usually present in crude oil. The arenes (aromatic hydrocarbons) constitute a smaller fraction of the total as compared with the alkanes and cycloalkanes. The prevalent constituents of the low-boiling cuts of petroleum are benzene, which is one of the simplest hydrocarbons, and its derivatives.

It is customary to classify the various 'crudes' according to their 'base' which may be one or several classes of hydrocarbons, whose content must be not less than 50%. Thus, there are paraffin-base (paraffinic) crude oil, naphthene-base (naphthenic) crude oil, paraffin-naphthene-base (paraffin-naphthenic) crude oil, paraffin-naphthene-aromatic-base crude oil, and aromatic-base crude oil.

Apart from the hydrocarbons, the organic part of petroleum contains pitch and asphalts which are high-molecular-weight compounds of carbon, hydrogen, sulphur and oxygen, and also sulphur compounds, naphthenic acids, phenols, nitrogen compounds such as pyridine and quinoline, various amines, etc. All of these substances are objectionable impurities, and their removal requires special facilities. Since they cause corrosion, the sulphur compounds are most detrimental both to the operation of the refinery units and the using equipment. In terms of sulphur content, petroleum is classed into low-sulphur (0.1-0.5% S), medium-sulphur (2.5-3% S), and high-sulphur (up to 5% S).

The inorganic impurities in crudes include water which may be present in a form easily separable from the petroleum by settling, and as part of stable emulsions. The water contains the dissolved inorganic salts NaCl, CaCl₂, MgCl₂, and some others. The ash content of crude oil is a few hundredths or even a few thousandths of one percent. There are also mechanical impurities in form of sand and clay particles.

Petroleum is separated into fractions by distillation. The composition of each fraction is related to its boiling range. Any two fractions falling in

the same boiling range are further classed in terms of density as light distillates and heavy distillates. The fraction make-up of a crude has a direct bearing on how it will be subsequently processed.

The properties of special importance to the processing and use of petroleum and its products are their pour point, flash point, fire point, self-ignition point, and explosiveness.

16.1 Key Petroleum Products

Petroleum processing yields liquid and gaseous fuels, lubricating oils and greases, solvents, the hydrocarbons ethylene, propylene, methane, acetylene, benzene, toluene, xylene and some others, solid and semi-solid mixtures of hydrocarbons (such as paraffin, petroleum jelly, and ceresin), petroleum asphalt, petroleum pitch, carbon black, naphthenic acids and their derivatives.

Liquid fuels produced by petroleum processing are classed into motor fuels and boiler fuels. In turn, motor fuels are classed into carburation or spark-ignition fuels, jet fuels, and Diesel fuels. The carburation or spark-ignition fuels include aviation and automotive gasolines and also the tractor fuels naphtha and kerosene. Jet fuels are kerosene fractions varying in composition or their mixtures with gasoline. The Diesel fuels include gas oil and solar oil — they are used in internal-combustion engines which operate by compression ignition. The boiler fuels are those which are burned by steamships, thermal power stations and industrial furnaces. The key boiler fuel is the heavy petroleum residuum.

Gaseous fuels are mixtures of petroleum hydrocarbons, used mostly in liquefied form for domestic needs. The most common product in this class is liquefied petroleum gas, or LPG for short. Its primary constituents are propane and butane in various ratios.

Lubricating oils provide for liquid film lubrication in machines. Some oils are used in power transmission systems, others as thermal and electric insulators (such as in transformers, power cables, and capacitors), and still others are used as the working fluid in brakes, hydraulic systems, steam-jet pumps, and elsewhere. It is customary to name them according to the purpose they serve. Thus there are transformer oils, capacitor oils, etc.

Greases are petroleum lubricants, solid or semifluid, comprising a thickening (or gelling) agent in a liquid lubricant. The thickening (or gelling) agents may be soaps, solid hydrocarbons or some other substances. Greases come in a wide variety of grades and classes, each adapted to a particular use. Some greases may be used in more than one service (universal greases), others only in very few (special grades of grease).

The *individual hydrocarbons* produced by processing crude petroleum and petroleum gases serve as feedstocks for the manufacture of polymers

and organic syntheses. The most important of them are the saturated hydrocarbons methane, ethane, propane, and butane, the unsaturated hydrocarbons ethylene and propylene, and the aromatic hydrocarbons benzene, toluene, and xylenes. Petroleum processing also yields high-molecular-weight saturated hydrocarbons (C_{16} and higher), such as paraffins and ceresins used in the manufacture of perfumes and as thickeners (gelling agents) for greases.

Petroleum asphalts produced from heavy petroleum residuum by its oxidation are used in road building, in the manufacture of roofing materials, as constituents for asphalt varnishes and printer's ink.

The principal products of petroleum refining are *motor fuels* which include aviation and automotive gasolines. An important property of a gasoline is its ability to resist detonation — a premature ignition in the combustion chamber. Knocking or pinging in the engine is an indication that the fuel has explosively ignited too early for the energy thus produced to be usefully consumed.

The antiknock quality of a fuel is stated in terms of its octane number or rating which is determined in a standard single-cylinder variable-compression engine. The octane number of a fuel is defined as the percentage (by volume) of isooctane (2,2,4-trimethylpentane) in the reference blend with *n*-heptane giving equal resistance to knock as the test fuel under standard test conditions. On an empiric scale adopted in 1927, the reference blends of *n*-heptane are assigned an octane number of 0 as they detonate with ease, and isooctane is assigned a value of 100 as it detonates with difficulty. If the test shows that the fuel of interest has the same resistance to knock as the reference blend of 80% isooctane and 20% *n*-heptane, it is assigned an octane number of 80. Since the octane scale was introduced, better reference blends than those containing isooctane have been found, and the octane scale has been extended to a value of 120.

Octane number tests have shown that the alkane series has an octane number which rises with increasing number of branches on the chain and decreases with increasing length of the hydrocarbon chain. The alkenes have a greater octane number than do the alkanes, and this number increases as the double bond shifts to the centre of the molecules. The cycloalkanes have a higher octane number than do the alkanes. The highest octane number has been found in the aromatic hydrocarbons. For example, *n*-propylbenzene has an octane number of 105, ethylbenzene has an octane number of 104, and toluene, an octane number of 107.

Gasoline produced by the straight distillation of crude oil consists mainly of alkanes with an octane number of 50-70. A higher octane number is assured through the improvement of straight-run gasoline by causing its hydrocarbons to form better structures and by the addition of what are called antiknock compounds — added in a ratio of not more than

0.5%, these substances markedly enhance the resistance of the fuel to knock.

The best known antiknock compound which dates back to the year 1923 is tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, although tetramethyl lead and some other lead alkyls are also used at present. The more recent additions to the antiknock agents include the carbonyls of the transition metals. The antiknock agents, including tetraethyl lead, are used in a mixture with ethylene dibromide, ethylene dichloride, or monochloronaphthalene which serve to prevent the build-up of lead in engines, for which reason they are called 'lead scavengers'. 'Leaded' gasoline, as the fuel thus treated is ordinarily called, is highly toxic and must therefore be handled with care.

16.2 Crude Oil Fractionation

Pretreating of crude oil. Crude petroleum contains dissolved 'petroleum' gases, water, inorganic salts and various mechanical impurities. Before a crude may be processed into products, it must be treated so as to remove foreign matter and to neutralize its chemically reactive impurities.

The associated petroleum gases are expelled by bringing down the pressure of the crude oil feed, thereby reducing the solubility of the gases. Thus recovered, the gases go to a step where they are processed to recover natural gasoline, ethane, propane, and butane. The remaining gases are removed from the crude in fractionating columns.

As the next step, the crude oil feed is passed to a tube-still furnace where it gives off its light gasoline fractions. Following that, the feedstock is mixed with a demulsifier and transferred to settling tanks where the crude gets rid of sand and clay, and its water settles out. At present, several techniques are used to break the emulsions and to remove the water, including a high-pressure thermochemical process. The emulsions can best be broken by introducing the emulsion into a high-potential electrostatic field set up by electrodes connected in a 30-45 kV a.c. circuit. The dewatering operation is accompanied by removal of a sizeable proportion of inorganic salts (desalting). Some desalters also perform a combination of thermochemical sedimentation and electrostatic demulsification.

The active impurities present in crude oil such as sulphur, hydrogen disulphide, salts and acids, are neutralized with alkali solutions or ammonia.

The preparation of a crude oil feedstock also includes the grading and blending of several crudes so as to obtain a feed having a more uniform quality.

Crude oil fractionation. This is the first step in petroleum refining. Crude fractionators are part of every petroleum refining complex. They in-

volve two operations, distillation and rectification, which are usually combined.

Distillation is an operation by which a mixture of mutually soluble liquids is physically separated into fractions, or cuts, according to their boiling points (or, rather, ranges) which are different for the various components and for the feed itself. At this step, the feedstock is raised to a boil and partly vaporizes — this produces an overhead product and a bottoms product, both differing from the feedstock in composition. At existing petroleum refineries, this is done in stills in a single pass. As a result, the low-boiling fractions passing into the vapour phase remain in the still and bring down the partial pressure of the vaporizing high-boiling fractions. Because of this, the operation may be carried out at a lower temperature.

The single-pass evaporation followed by vapour condensation produces a light fraction and a heavy fraction. The light fraction is higher and the heavy fraction is lower in the low-boiling constituents than the feed. In other words, one fraction is enriched with low-boiling components and the other fraction with high-boiling components. However, this operation fails to fractionate the crude to the desired degree and to yield the products that boil within the specified temperature ranges. For this reason, it is followed by rectification.

Rectification is a diffusion operation which has as its objective to separate liquids according to their boiling points by causing the vapour and the liquid to come in contact countercurrent repeatedly.

Crude fractionation systems may be single-stage or double-stage, with the required heat supplied by direct-fired furnace-type tubular heaters, also called pipe (or tube) stills. Furthermore, they may operate at atmospheric pressure or under a vacuum, depending on the overall plant layout and the quality of the crudes coming in for refining. Sometimes, a crude fractionation system may combine operation at atmospheric pressure, known as atmospheric distillation, and under a vacuum, known as vacuum flashing.

The flowsheet in Fig. 16.1 represents a two-stage crude fractionation unit combining atmospheric distillation and vacuum flashing. As is seen, the crude to be fractionated is passed through heat exchangers where it is heated to 170-175 °C by the outgoing streams (heat recovery) and enters a tubular heater, 1. Heated to 350 °C, the feedstock is introduced to the middle evaporating portion of an atmospheric fractionator, 2. Here the feedstock is vaporized in a single pass. As the hot feedstock enters the tower, it instantaneously vaporizes due to an abrupt fall in pressure; in doing so, it expends some of its heat. The low-boiling vapours pass upwards and come in contact with the liquid, called the reflux, which flows continuously by gravity in the downward direction. When they come in contact with the reflux, the vapours are cooled and partly condensed. In contrast, the reflux is heated and the most volatile of its fractions are evaporated.

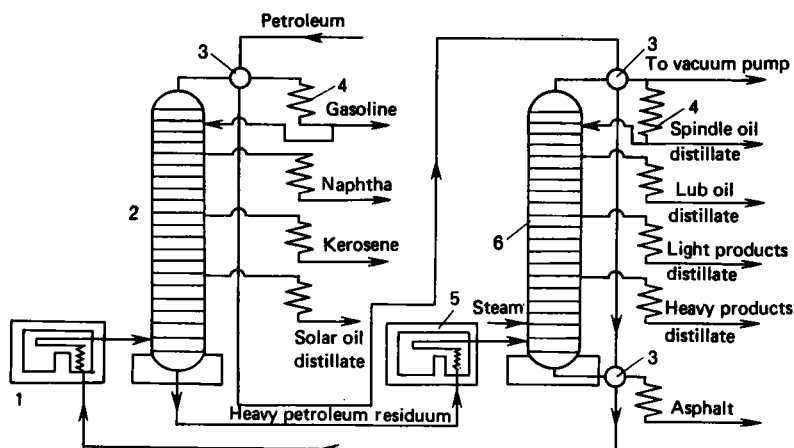


Fig. 16.1 Flowsheet of an atmospheric-vacuum crude oil fractionation plant:

1, tubular heater; 2, atmospheric fractionator; 3, heat exchangers; 4, condensers; 5, tubular heater; 6, vacuum flasher

Thus, the liquid stream is enriched with the less volatile components and becomes heavier, and the vapours are enriched with the more volatile components and become progressively lighter. This countercurrent action results in fractional distillation — physical separation of hydrocarbons on the basis of their boiling ranges. The desired fractions may be drawn off as net products at appropriate points, or trays, of the tower within the specified temperature ranges. Thus, solar oil condenses and is drawn off at 300-350 °C, kerosene at 200-300 °C, and naphtha at 160-200 °C. The fraction leaving the tower at its top, the overhead product, contains vaporized gasoline which is cooled and condensed in heat exchangers, 3 and 4. Some of the liquid gasoline is used as reflux to irrigate the atmospheric tower, 2. The product collecting at the base of the atmospheric fractionator and aptly called the *atmospheric residue* (or the *topped crude oil*) is further fractionated in the second tower, 6, the vacuum flasher. Vacuum is used in order to prevent the cleavage of the hydrocarbons at elevated temperatures. Before it enters the vacuum flasher, the atmospheric residue is passed through a second tubular heater, 5, where it is heated to 400-420 °C. The vapours formed in the heater are introduced into the vacuum flasher where the pressure is maintained at 5.3-8.0 kPa. Here, steam is used to strip the descending unvaporized liquid of its more volatile components so as to ease their vaporization and to bring down the temperature at the base of the flasher. The range of products into which the atmospheric residue is separated in the vacuum flasher depends on whether the unit is designed to produce lubricating oils or fuels. In the former case, the products are light, medium and heavy lube oil distillates. In the latter case,

there is only one product drawn off — vacuum, or heavy, gas oil used as the feedstock for catalytic cracking and hydrocracking. The lube oil distillates are purified and blended in various ratios to produce several grades of lubricating oils. The nondistillable pitch products (asphalt and residual oil) withdrawn from the base of the vacuum flasher are used as the feedstock for further processing by thermal cracking and the production of coke, bitumen, and high-viscosity oils.

The yield of a fractionation plant depends on the composition of the crude and the plant configuration. The same crude may be turned into various products when processed by the various units of the same petroleum refining complex.

16.3 Destructive Petroleum Processing

Crude fractionation physically separates crude petroleum into its constituent fractions. Before these fractions can become usable products in addition to those listed above, they have to be subjected to whatever chemical modifications may be necessary. These chemical modifications constitute what we will call the destructive methods of petroleum processing.

16.3.1 Thermal Processes

The first to be commercialized among the destructive methods of petroleum processing have been thermal processes in which the hydrocarbons are broken up into the lower-molecular-weight components by heat. Among them are thermal cracking, pyrolysis, and thermal coking.

The kinetics and mechanism of the thermal processes. Petroleum consists of a very great number of individual hydrocarbons, so the reactions that its components may undergo at elevated temperature are many and diverse. The thermal decomposition of the molecules is accompanied by synthesis and, in part, by isomerization, with many of these reactions being reversible. By applying the laws of chemical thermodynamics, we may predict the probability of a particular reaction, the maximum conversion, and the equilibrium composition of the products.

The manner in which the free energy change in the formation of some hydrocarbons depends on temperature is shown in Fig. 16.2. As is seen, the thermodynamic stability of the hydrocarbons, except acetylene, C_2H_2 , decreases with increasing temperature while that of the homologues falls with a rise in molecular mass. At elevated temperatures, the arenes are much more stable than the alkanes and cycloalkanes.

At present it is customary to think of the thermal reactions of hydrocarbons as proceeding by the free-radical mechanism which involves three stages, namely: chain initiation, chain propagation, and chain termination.

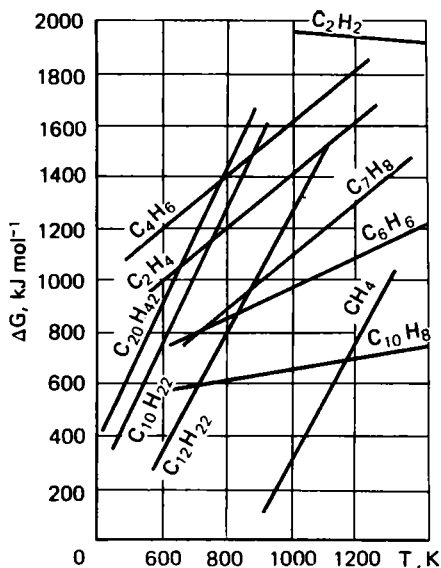
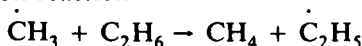


Fig. 16.2 Gibbs free energy change as a function of temperature for the formation of hydrocarbons from simple substances

Chain initiation. This stage, or the decomposition of hydrocarbons, predominantly occurs at a C—C bond. No C—H bond is ruptured because substantially more energy would have been necessary for this to occur. The energy of a C—C bond is 360 kJ mol^{-1} , and that of a C—H bond is 412 kJ mol^{-1} . The C—C bonds in the cycloalkanes are not so strong as they are in the normal alkanes. The C—H and C—C bonds in the arenes are stronger than they are in the alkanes, but the bonds conjugate on an aromatic ring are weakened. The ring conjugation reduces the bond strength in about the same proportion as the conjugation with a double bond.

Chain propagation (free-radical reactions). The unsaturated groups of atoms or ions which contain one or more unpaired electrons, that is, which do not have their full complement of electrons, and do not decompose instantaneously to more stable species are called free radicals. As a result of an incomplete valence shell, free radicals are highly reactive, and the reactions involving them proceed at a very high rate. On colliding with the molecules of the feedstock, they form a product plus yet other free radicals, and this process, once initiated, can be repeated over and over, making the reaction self-propagating. The life time of free radicals is very short, being of the order of 10^{-3} – 10^{-4} s. The entire series of reactions that follows the production of the very reactive intermediates, or free radicals, is called a chain reaction. The bulk of the reaction product results precisely from a chain reaction via the free radicals rather than from the rupture of the carbon chain. The reactions involving free radicals are as follows.

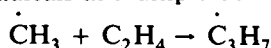
(1) The substitution reaction



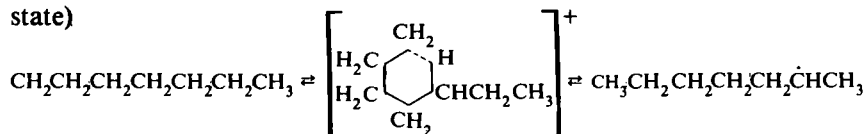
(2) The decomposition of free radicals with the formation of unsaturated molecules plus more free radicals



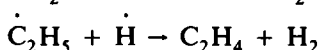
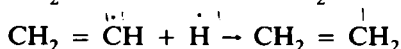
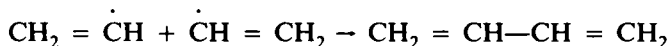
(3) The addition of radicals at multiple bonds



(4) Isomerization (presumably, it proceeds via an intermediate cyclic state)



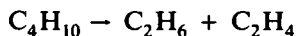
Chain termination. At equilibrium, the probability of a free radical meeting another free radical becomes comparable with the probability of their collision with the molecules of the feedstock. The interaction of two free radicals leads to what is termed chain termination, with the formation of a stable hydrocarbon:



The reactions involved in the thermal decomposition of hydrocarbons can be described by first-order rate equations. However, a complete mathematical description of the entire complex of thermal reactions is out of the question because even in the case of the simplest hydrocarbons the thermal decomposition involves a multiplicity of elementary steps. Also, the kinetics of chain reactions is affected by the reaction products.

In the pages that follow we will examine the thermal modification of hydrocarbons in the gas phase. As follows from Fig. 16.2, the hydrocarbons may be ranked in terms of thermal stability at elevated temperatures in the following sequence: alkanes — cycloalkanes — alkenes — arenes.

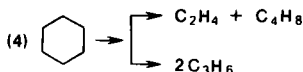
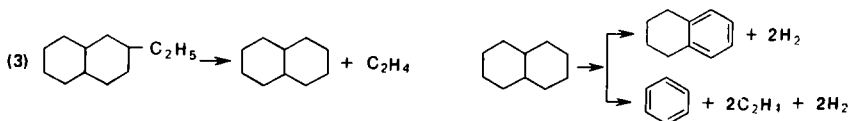
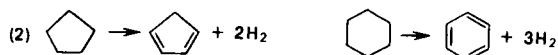
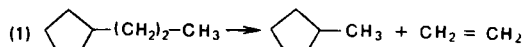
Thermal modification of alkanes. The chain of a normal hydrocarbon is usually ruptured at the middle with the formation of a saturated and an unsaturated hydrocarbon; this may be accompanied by dehydrogenation:



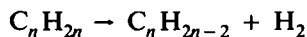
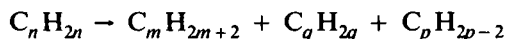
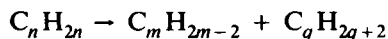
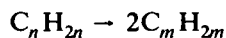
Thermal modification of cycloalkanes. Thermodynamically, the

following reactions are most typical:

- (1) dealkylation, or shortening, of the paraffin side chains;
- (2) dehydrogenation of the ring with the formation of cycloalkenes and aromatic hydrocarbons;
- (3) partial or complete decyclization of polycyclic hydrocarbons following the dealkylation step;
- (4) decomposition of monocyclic hydrocarbons into alkenes and alkanes:

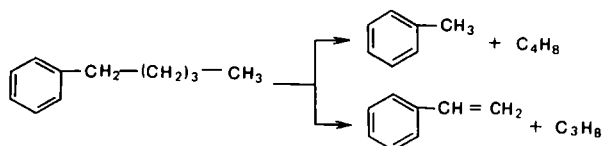


Thermal modification of alkenes. Alkenes are not present in the cracking feedstock, but they are formed as other classes of hydrocarbons undergo thermal decomposition, and their thermal modification has a vital bearing on the make-up of the cracked products. The decomposition of alkenes may follow several routes:

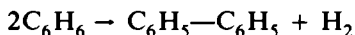


The higher alkenes come very close to the higher alkanes in terms of thermal stability.

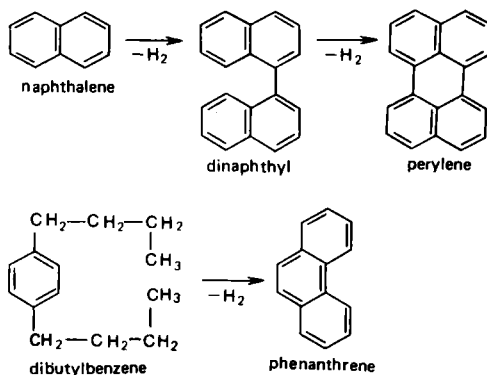
Thermal modification of arenes. The arenes are thermally most stable of all hydrocarbons, but their thermal stability strongly depends on their structure. Arenes with long side chains are capable of dealkylation:



In thermal processes, the unsubstituted arenes undergo dehydrocondensation and densification by a chain mechanism. Benzene condenses according to the scheme



As the reaction progresses, the condensation of various cyclic hydrocarbons leads in the long run to the formation of carboids (coke). The gradual increase in the molecular mass and carbon content and the loss of hydrogen as a result of the condensation of aromatic structures may be illustrated as follows



Coking is objectionable unless the process is effected in order to produce petroleum coke.

To sum up, the destructive processing of petroleum involves the following typical reactions: dealkylation, polymerization, alkene cyclization, cycloalkane decyclization, destructive condensation of alkenes, arene condensation, and high-level densification to coke. Which of these reactions predominates and how far it proceeds determines the qualitative and quantitative make-up of the end products.

Thermal cracking. It is effected at a temperature of 470–540 °C and a pressure of 2–7 MPa. The thermal decomposition of the hydrocarbon stock commences at 380–400 °C. As the temperature rises, the cracking rate builds up heavily because the process occurs within the kinetic region. With the pressure and conversion held constant, an increase in temperature results in a higher percentage of light components in the products, a reduced yield of the heavy fractions, and a smaller quantity of coke. At the same time, the yield of the gas is markedly increased, and so is the percentage of unsaturated hydrocarbons in it.

As the process pressure rises, the boiling point of the stock and of the cracked products also rises. By varying the process pressure, it is possible to control the phase make-up in the cracking zone and to effect the crack-

ing operation in the vapour, liquid, or mixed phase at will. Vapour-phase cracking is usually applied to gasoline and kerosene-gas oil fractions. In the case of vapour-phase cracking, the process pressure has a decisive effect on the make-up of the cracked products because a rise in pressure speeds up the secondary reactions, such as the polymerization and hydrogenation of unsaturated hydrocarbons, condensation of aromatic hydrocarbons, and some others. The gas yield is then reduced.

In contrast, pressure has but a negligible effect on the liquid-phase cracking of heavy feedstocks (such as heavy petroleum residuum and pitch). In the case of mixed-phase cracking, high pressure favours the homogenization of the stock — the gas is partly dissolved in the liquid, thereby reducing its density, but the gas phase gains in density. Importantly, operation at elevated pressure needs smaller reaction vessels.

The key products of thermal cracking are hydrogen gases used as feedstocks for petrochemical syntheses, cracked gasoline, the kerosene-gas oil fraction, thermal gas oil, and cracking residue. Cracked gasoline has a low thermal stability and a low octane rating (66-68). In terms of its antiknock quality, it falls short of the requirements to be met by acceptable fuels for automobile engines. Before it can be used as an automotive fuel, cracked gasoline has to be stabilized.

The kerosene-gas oil fraction (200-350 °C) is a valuable component of fuel oil for marine engines. After hydrotreating, gas oil may be used as a component of Diesel fuel.

Thermal gas oil is used as the feedstock for the production of carbon black.

The thermal cracking residue (over 350 °C) is used as fuel for thermal power stations, power ships, and industrial furnaces. It is higher in quality as a fuel than the straight-run residuum. It has a higher calorific value, a lower congelation point, and a lower viscosity which is especially important as this makes it easier to convey the fuel over pipelines and to atomize it in burners.

As a way of increasing the yield of the thermal cracking residue, some petroleum refineries process the pitch coming from most vacuum-flashing units in a thermal cracking unit under relatively mild conditions to reduce its viscosity — a process known as *visbreaking* (from 'viscosity breaking').

Thermal cracking may be applied to a wide range of feedstocks — from light straight-run gasoline to pitch and the heavy residue stocks of secondary origin, such as are left over from catalytic cracking and thermal coking.

The arrangement of a thermal cracking plant depends on the stock used. A feature common to the earlier types of plant is provision of a tubular heater. It serves not only to heat and vaporize the stock partly or completely, but also to effect some chemical changes. In this, it differs

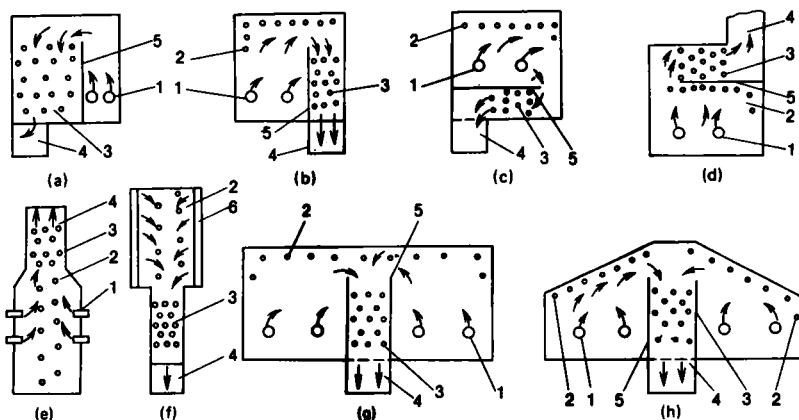


Fig. 16.3 Basic types of tubular heaters:

(a) convection type; (b) single side convection chamber; (c) single bottom convection chamber; (d) single top convection chamber; (e) vertical cylindrical convection chamber; (f) surface-combustion convection chamber; (g) horizontal-arch two-chamber double-stream type; (h) sloping-arch two-chamber double-stream type; 1, burners; 2, radiation coil; 3, convection coil; 4, flue; 5, overflow partition; 6, panel burners

from the tubular heater, or pipe still, of crude oil fractionation units. Owing to the high temperature and pressure, the stock is cracked directly in the coil tubes. Since the tubes are of small diameter, the resulting vapour-liquid mixture is rapidly withdrawn from the high-temperature cracking zone where the risk of a fire and / or explosion is high. For a higher conversion of the stock, most thermal cracking units of this type have chambers, or tanks, to reclaim the heat of the cracked products leaving the coils. Since the chambers are large in volume, the products may stay there for a long time (up to 100 s), and this enhances the degree of cracking.

The key types of tubular heaters are shown in Fig. 16.3.

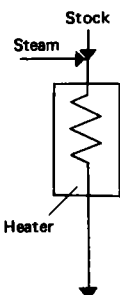
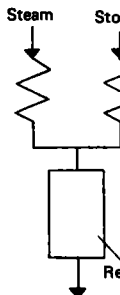
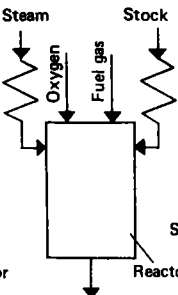
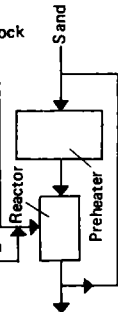
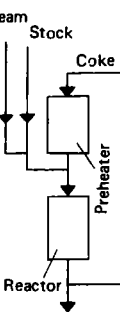
The newer thermal cracking units operate with a recycle.

Pyrolysis. This is the most severe of all thermal cracking processes. It is effected at 700-1000 °C and a pressure close to atmospheric. It produces valuable lower alkenes (olefins) which are used as the feedstock for petrochemical syntheses.

The best stock for the production of alkenes are alkanes. When a normal alkane is cleaved, the following events take place: almost all of the ethane is converted to ethylene, the propane and butane are converted to a high degree to ethylene and propylene, while the hydrocarbons higher than C₄ give ethylene, propylene, and C₄ and higher alkenes. When isoalkanes are pyrolyzed, the ethylene yield is lower and more gaseous alkanes are produced, notably methane. When the process is effected at moderate

Table 16.1 Classification of Pyrolysis Units by Form of Heat Transfer

T204

Coil-heater type	Homogeneous	Autothermal	Solid heat-transfer agent	
			sand	coke
				
Heat transfer through wall	Stock mixed with steam	Direct contact of stock with combustion products	Direct contact of stock with solid heat-transfer agent	

temperatures, the arenes are a ballast. When the process conditions are more severe, they are largely converted to coke and pitch.

The level of pyrolysis is decided by temperature, contact time, and pressure. High temperature favours pyrolysis. Thus, an increase in temperature in the pyrolysis of propane will bring about an increase in the yield of ethylene and propylene. Since the yield of propylene reaches a maximum at a lower temperature, the ethylene:propylene ratio in the product can be varied at will. This ratio can also be adjusted by varying the contact time. Pyrolysis under severe conditions (at a temperature of over 800 °C and a contact time of 0.3-0.4 s), widely practiced recently, provides for a high yield of ethylene.

When the process pressure is raised, the alkene content of the product is reduced and that of *n*-alkanes and aromatic hydrocarbons is increased. As a rule, the pressure at the exit from the coil of the pyrolysis unit heater is 0.03-0.12 MPa, but it is desirable to bring down the pressure still more. The partial pressure of the hydrocarbons is reduced by adding steam to the stock and by using suitably configured coils. The addition of steam to the stock raises the yield of ethylene, reduces coke formation on the tube walls, and raises the velocity at which the feed gas mixture moves in the tubes. In

block-diagram form, pyrolysis units are shown in Table 16.1 along with the heat flows.

In recent years, quite a number of new pyrolysis processes have been developed, among them pyrolysis over a catalyst and with an initiator, pyrolysis in the presence of hydrogen, and in molten heat-transfer agents.

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Thermal coking. Thermal coking is a process by which the stock is decomposed as far as practicable in the absence of air in order to produce petroleum coke and a distillate containing a wide range of fractions. This process converts to light petroleum products not only heavy straight-run residual stocks, such as residuum and pitch, but also asphalt and residues from lube oil production. Apart from ash-free petroleum coke, the products of the process include gas, gasoline, Diesel oil, and furnace fuel oil.

Petroleum coke is used as a reducer in the chemical process industries, as one of the major raw materials for the manufacture of carbon electrodes in the aluminium and other electrometallurgical industries, in the manufacture of abrasives (SiC , B_4C , and TiC), additives for aerospace applications (Be_2C and TiC), nuclear-power uses (B_4C and ZrC), and as a raw material for carbon materials used to line chemical equipment. If it meets purity and other required specifications, it goes to make graphite blocks used as neutron moderators in nuclear reactors.

In liquid-phase thermal coking processes, coke is formed as a result of the following sequence: arenes $\rightarrow$ pitch $\rightarrow$ asphaltene $\rightarrow$ coke $\rightarrow$ graphite.

Three types of thermal coking processes are used commercially: (1) a batch technique, (2) a cyclic, semicontinuous process, variously named *delayed coking*, *decarbonizing* or *low-pressure coking*, and (3) a continuous technique. The process most widely practised at present is the cyclic, semicontinuous process effected in *delayed coking units*. Here, the process goes on at a temperature of 505-515 °C and a pressure of 0.2-0.3 MPa. This process is a batch one as far as coke removal is concerned, and continuous with regard to charging the feedstock and withdrawal of the distillates.

In continuous coking, the hot feedstock is brought in contact with the fluidized bed of a hotter heat-transfer agent. Quite aptly, this technique is known as the *continuous fluid coking process*. The heat-transfer agent most commonly used at present is a circulating stream of coke particles serving as seeds, transported by an air stream.

Delayed coking units and continuous fluid coking units show about the same economic performance. The delayed coking process, however, gives a greater yield of coke.

16.3.2 Thermocatalytic Processes

Thermal processes were a sole choice for the destructive processing of petroleum until 1940. Since then, quite a number of thermocatalytic pro-

cesses, such as catalytic cracking, catalytic reforming, hydrogenolysis of sulphur compounds, etc., have been developed which are currently processing between them 90% of the total petroleum. Owing to catalysts, these processes give a markedly higher yield of valuable products of a better quality and produce substantially more aromatic hydrocarbons for use by the chemical process industries. Catalytic processes need far less energy than thermal processes. Also, they proceed at a higher rate and at lower temperatures and pressures. Chronologically, the first to be commercialized has been catalytic cracking.

Catalytic cracking. The earliest catalysts used in this process were specially treated natural clays — amorphous alumina silicates answering the general formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O} + n\text{H}_2\text{O}$. These catalysts are of poor thermal stability and give a low yield of gasoline — not more than 20-30% by weight.

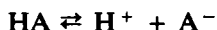
Today natural alumina silicates have all but been ousted by synthetic crystalline catalysts consisting of modified hydrated alumina silicates and 5-20% zeolites. With these zeolitic catalysts, the yield of gasoline has been raised to 45-50% without any impairment in overall performance.

Catalysts for catalytic cracking are required to be mechanically robust, to resist abrasion and attack by steam, and to be insensitive to elevated temperature and sudden temperature changes.

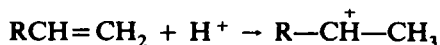
A major drawback of catalysts for catalytic cracking is the rapid loss of activity. The pores of catalyst grains are plugged with coke in a matter of 10-15 minutes of operation. Therefore, the cracking operation proper has to be alternated with regeneration which consists in that the catalyst is blown over with air at 540-580 °C in order to burn the coke and gum deposit off its surface. The air is usually diluted with inert gases as a precaution against local heat build-ups.

The reactions involved in catalytic cracking proceed by the carbonium-ion mechanism. The reactions that occur in catalytic cracking include alkylation, dealkylation, isomerization, polymerization, and hydrogenation, among others.

The mechanism of catalytic cracking may be visualized as a sequence of the following chain reactions. The chain initiation step occurs under the influence of the hydrogen ion of the catalyst:



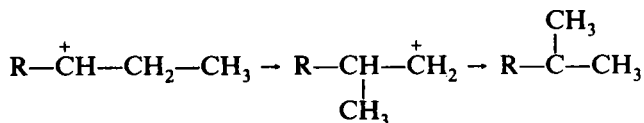
where HA represents the aluminosilicate catalyst as an acid. The carbonium ions are best formed when the protons of the catalyst react with alkenes:



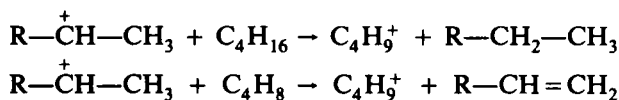
This mechanism has been proved by experiments using deuterium to label the atoms.

The following transformations are most typical for carbonium ions.

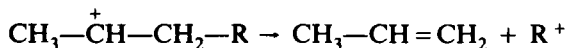
(1) Re-arrangement of the atoms in the hydrogen molecule or in the methyl group (skeleton isomerization):



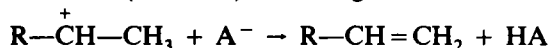
(2) The reaction with neutral molecules with the formation of more carbonium ions:



(3) The decomposition of the carbonium ions containing a large number of carbon atoms:



The chain propagates via various transformations of the carbonium ions and hydrogen exchange with neutral molecules. The chain termination takes place due to the reaction between the carbonium ion (a cation) and the aluminosilicate ion (an anion) according to the scheme:



In the long run, the catalyst restores its chemical composition, and the process takes place all over again.

Catalytic cracking markedly differs in mechanism from thermal cracking due to both the action of the catalyst and the kinetic factors. The mechanism of catalytic cracking may be summed up as follows.

1. The various classes of hydrocarbons in terms of their tendency to undergo the reactions of catalytic cracking line up in a sequence which is different from that associated with thermal cracking. Taking the basic groups of hydrocarbons as examples, this sequence in decreasing order of their tendency to react looks like this:

Thermal cracking: alkanes > cycloalkanes > alkenes > alkylated arenes.

Catalytic cracking: alkenes > highly branched arenes > cycloalkanes > alkanes.

This ordering is due to the selective adsorption of the various hydrocarbons on the surface of the catalyst. The first to be adsorbed on the catalyst are the highly energetic unsaturated compounds, such as dialkenes, alkenes, and arenes. The alkanes come last in this sequence. In the case of alkenes and arenes, the catalyst speeds up the cracking reactions by a factor of several hundred or even thousand more than it does in the case of alkanes. Selective adsorption is responsible for the stepwise sequential

course of the process in which the hydrocarbons strongly sorbed by the catalyst tend to retard the cleavage of the poorly sorbed hydrocarbons. In thermal cracking, all the components of the feedstock undergo transformations simultaneously.

2. The disproportionation of hydrogen takes place. The hydrogen molecules adsorbed on the catalyst tend to be dehydrogenated, which fact leads to a greater unsaturation and, as a consequence, to a stronger adsorption on the catalyst. As a result, the newly formed alkenes begin to polymerize and form coke which is the final product of the process. As this happens, the hydrogen lost by the molecules adsorbed on the catalyst saturates the various molecular fragments, above all the isomerized alkenes. Thus, some molecules lose their hydrogen while others gain it, and this is the essence of disproportionation. Gradually, coke covers all of the active sites on the catalyst, and this necessitates its regeneration. Coke is an unavoidable co-product of primary catalytic cracking while in thermal cracking it results from secondary chemical changes and is the product of the side high-temperature reaction of condensation.

3. Isomerization plays an important role. As the unsaturated fragments are isomerized and gain more hydrogen, the cracked products accumulate a progressively larger proportion of isoalkanes which is the reason why the cracking gas is so high in isobutane.

The above features of the mechanism by which catalytic cracking occurs have a vital bearing on the composition and properties of the cracked products. Among other things, the gas carries less low-molecular-weight components, but more isobutane. Catalytically cracked gasoline is high in isoalkanes and aromatic hydrocarbons.

The major advantages of catalytic cracking over thermal cracking are the higher reaction rate in the presence of a catalyst and the more valuable products.

A comparison of catalytic and thermal cracking is given in Table 16.2.

Catalytic cracking is effected in units which may use a moving bed of spherical catalyst grains or a fluid bed of a catalyst in the form of spray-dried microspheres (20-80 μm in diameter) or irregular pulverized particles (12-120 μm across). The flowsheet of a moving-bed catalytic cracking unit which uses a zeolitic catalyst is shown in Fig. 16.4, and that of a fluid-bed (or simply fluid) catalytic-cracking unit in Fig. 16.5. Of the two types, the latter is more commonly used.

Referring to Fig. 16.5, the feedstock is heated in a furnace-type heater, 1, mixes with recycle, and enters the riser of a catalyst-conveying line over which the catalyst, feedstock and recycle are fed to a reactor, 3. The cracking reaction commences in the riser and reaches completion in the reactor. The cracked vapours and the steam fed to the stripping section of the reactor leave it through a port at the top and are passed to the base of a frac-

Table 16.2 Comparison of Thermal and Catalytic Cracking

Process particulars	Thermal cracking	Catalytic cracking
Temperature, °C	470-540	450-525
Pressure, MPa	2.0-2.7	0.06-0.14
Products:		
gas	Mainly the C_1 - C_2 fraction	Mainly the C_3 - C_5 fraction
gasoline	Sizeable proportion of normal alkanes, alkenes and dienes. Antiknock rating, 66-68	Sizeable proportion of highly branched alkanes and arenes. Antiknock rating, 78-85

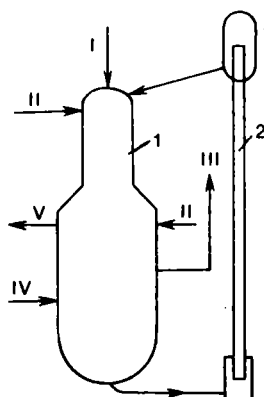


Fig. 16.4 Moving catalyst bed unit:

1, integral reactor-regenerator; 2, airlift; I, feedstock; II, steam; III, flue gases; IV, air; V, reaction products

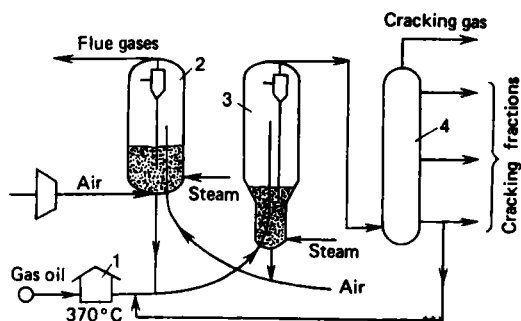


Fig. 16.5 Fluid-bed catalytic-cracking unit:

1, furnace-type heater; 2, fluid-bed regenerator; 3, upflow reactor; 4, fractionator

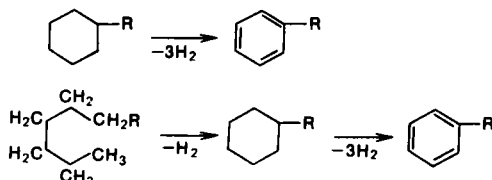
tionator, 4. The gas, water vapours and gasoline vapours are withdrawn from the top of the fractionator. A pump withdraws the heavy gas oil with catalyst fines suspended in it from the base of the fractionator.

The catalyst slowly sinks from the fluidized bed of the reactor to the stripper which receives steam for removal of petroleum products off the surface of the charge. The catalyst then passes into the riser whence an air stream lifts it to a regenerator, 2. The bulk of the air required to burn out the coke is fed directly to the regenerator. Excess heat is reclaimed by feeding steam or water into the regenerator coils. The flue gases produced by burning out the coke are withdrawn at the top and passed to an electrostatic precipitator to catch catalyst fines.

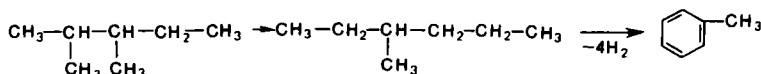
Among the more recent additions to catalytic cracking are upflow expanded (or ebullated) bed reactors.

Catalytic reforming. This process has as its objectives to upgrade the antiknock rating of the gasoline fractions and to produce arenes which are valuable feedstocks for petrochemical syntheses.

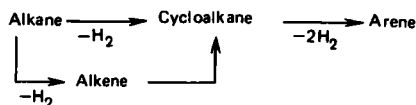
This process re-arranges, or *reforms*, the molecular structure of hydrocarbons without changing the number of atoms in a molecule. The reactions lying at the basis of catalytic reforming are the dehydrogenation of cycloalkanes (naphthenes) and the dehydrocyclization (that is, dehydrogenation associated with cyclization) of alkanes.



If the original alkane has fewer than six carbon atoms in the main chain, the aromatization is preceded by the isomerization of the alkane with more functional groups added to the chain:

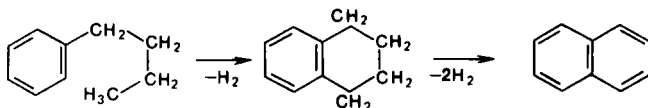


Presumably, the dehydrocyclization follows two pathways:



As a result, the cycloalkanes are dehydrogenated with the formation of aromatic hydrocarbons whose yield increases with increasing temperature and decreasing pressure. In catalytic reforming, the aromatization of the cycloalkanes is the most desirable reaction.

The dehydrocyclization of the alkyl-aromatic hydrocarbons produces condensed aromatic systems:



The desired reactions of catalytic reforming examined above are accompanied by side reactions which are often undesirable. Thus, some of the higher hydrocarbons are cracked with the formation of the gaseous lower alkenes and alkanes:



which is then followed by the hydrogenation of the alkenes:



Thus is the reason why the gases from catalytic reforming consist almost exclusively of alkanes noticeably diluted with hydrogen.

Another objectionable reaction is the dehydrocondensation of the aromatic hydrocarbons with the formation of polycyclic and condensed compounds. Because of this, the catalyst is contaminated with a sizeable amount of coke. Since dehydrocondensation is a reversible reaction, the coke formation can be suppressed and the service life of the catalyst can be extended by effecting catalytic reforming with the hydrogen maintained under an elevated pressure. One of the catalytic reforming processes commercialized first has been *hydroforming* which is effected in a hydrogen environment at a pressure of 1.5-2.5 MPa and a temperature of 480-550 °C over a molybdenum catalyst on an alumina base.

The commercial catalysts for catalytic reforming include platinum (applied to an alumina base and promoted with fluorine or chlorine, or aluminosilicate, or zeolite, etc.), and polymetallic catalysts made of platinum alloyed with rhenium, iridium, cadmium, palladium or germanium (using the same bases). It has also been proposed to use the rare elements yttrium and cerium as promoters to enhance the activity, selectivity and thermal stability of catalysts.

Of all the catalysts, the one most commonly used is platinum on an alumina base, and the process in which it is used is known as the *platforming* (that is, platinum reforming) *catalytic process*. The platforming catalyst contains 0.3-0.65% platinum. A high-platinum catalyst has a higher activity and enhances the octane rating of the reformed gasoline. The factors limiting the platinum content of the catalyst are the increase in the rate of the demethylation and cleavage of the cycloalkanes leading to a reduced yield of gasoline, and the high cost of platinum.

Platforming catalysts can operate consistently without regeneration during 6 to 12 months. Unfortunately, they are highly sensitive towards sulphur and nitrogen compounds, lead, and arsenic. Moisture in the

feedstock is likewise an objectionable impurity as it reacts with the chlorine promoter of the catalyst. The hydrogen chloride thus formed strongly attacks the equipment. As a way of extending the service life of the catalyst, the feedstock for platforming is subjected to hydrotreating and drying. The spent catalyst is regenerated by slowly burning out the coke.

Polymetallic catalysts are as stable as the bimetallic catalysts, but have a higher selectivity and efficiency. The stability of a catalyst is improved by adding to it an amount of rare-earth elements which provide for the high dispersion of the platinum. Catalysts have been developed which are less critical with regard to the percentage of moisture, sulphur and nitrogen in the feed.

The main products of the process are the hydrogen-carrying gas and a liquid fraction called the *reformate*. Some of the hydrogen is used to make up for the losses in the recycled hydrogen-bearing gas, but its greater proportion is routed to hydrocracking and hydrotreating units. The yield of 90% by volume hydrogen from the platforming catalytic reforming process is 0.7-1.5%.

The reformate is used as a high-octane component of gasoline for automobile engines (with an octane rating of 95) or processed to recover its arenes. The individual arenes that can be recovered from the gasoline produced by platforming include benzene, toluene, ethyl benzene, and all the feedstocks for organic syntheses. The hydrocarbons are recovered by extraction.

The platforming catalytic reforming process is carried out at a temperature of 470-540 °C and a pressure of 2-4 MPa in a hydrogen-rich environment. The principal reactions involved in this process are reversible and endothermic, and the process as a whole is likewise endothermic. In consequence, when the process is effected in a fixed-bed reactor, the temperature gradually declines on moving down the stream. The fall in temperature might lead to a decrease in the equilibrium conversion and reaction rate. To counteract this effect and to improve the process conditions, platforming is carried out in a triple-reactor unit, with the charge heated before it enters each reactor to compensate for the endothermic reactions that occur. One such reaction is dehydrogenation during which the charge rapidly cools. The first reactor on the stream should hold a lesser quantity of catalyst than the remaining two reactors because the reactant concentration in the charge is high, the reactions proceed at a very high rate, and the endothermic effect is especially noticeable. The total catalyst is shared among the reactors in a 15:35:50 ratio. In the last reactor which holds half the total catalyst, the temperature changes least of all because there is an increase in the yield of hydrocracking products, and this is accompanied by the evolution of heat. The operating conditions of a triple-reactor platformer are listed in Table 16.3.

Table 16.3 Operation of a Triple-Reactor Platformer

Particulars	Reactor		
	1	2	3
Temperature, °C			
inlet	502	502	502
outlet	433	472	496
Temperature drop, deg. C	69	31	6
Catalyst, % of the total charge	15	35	50
Octane number	65.5	79.5	90.0
Main reactions	Dehydrogenation, dehydroisomerization	Dehydrogenation, dehydroisomerization, hydrocracking, dehydrocyclization	Hydrocracking, dehydrocyclization

Other modifications of catalytic reforming involve the use of cyclic and fluid-bed units of the regenerative type in which the catalyst is cyclically or continuously circulated through the system and regenerated in a separate vessel.

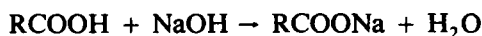
16.4 Purification of Petroleum Products

As they emerge from a processing unit, petroleum products are mostly not marketable products because they carry all kinds of impurities impairing their quality and rendering them unstable.

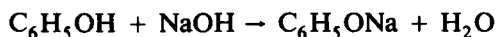
The objectionable impurities can be removed by chemical and physico-chemical methods, such as treatment with alkalis and sulphuric acid, deparaffinization with urea, adsorption, catalytic treatment, solvent extraction, etc.

Alkali treatment has as its objective to remove naphthenic and fatty acids, phenols, hydrogen sulphide and mercaptanes.

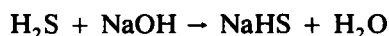
The free acids of the product being treated react with the alkali to form salts (soaps):

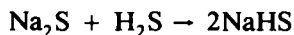
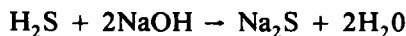


The phenol reacts with the alkali to form phenolates:

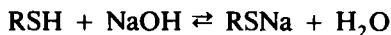


The hydrogen sulphide reacts with the alkali to form acid and neutral salts:



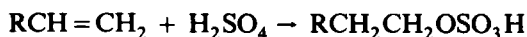


The mercaptanes react with the alkali to give mercaptides:



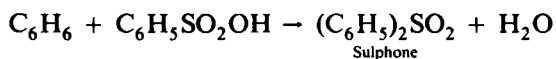
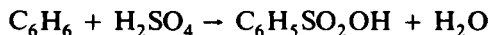
One of the bottlenecks of alkali processing has until recently been final removal of moisture from the processed distillate. This problem has been resolved by adding an electrostatic precipitator to the plant. Among the drawbacks of alkali processing are the irrecoverable loss of the expensive reactant and the formation of wastewater high in sulphur and alkali which are difficult to reclaim.

Treatment with sulphuric acid is employed to remove alkenes, arenes, resinous, nitrogen and partly sulphur compounds. The alkenes react with the sulphuric acid to form acid and neutral esters:



The acid esters dissolve in the sulphuric acid, and the neutral esters in the refined product, so their formation is undesirable.

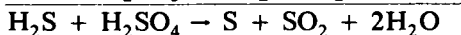
The arenes can only be sulphurized with concentrated sulphuric acid taken in an excess over its stoichiometric quantity. The reaction yields sulphoacids and sulphones soluble in sulphuric acid:



Sulphone

All of the resinous substances usually pass into acidic pitch which is in effect the spent acid with the reaction products dissolved in it.

The hydrogen sulphide is oxidized with the formation of elemental sulphur and sulphur dioxide:



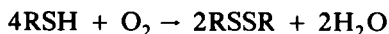
The mercaptanes react with sulphuric acid to form disulphides and sulphur dioxide:



Sulphuric acid treatment requires bulky equipment, a large number of reactants, etc.

Adsorption and catalytic processing. Adsorption is used to remove unsaturated hydrocarbons from aromatic hydrocarbons, and also resinous substances, asphaltenes and other objectionable compounds from light petroleum products. The most commonly used adsorbents are natural clays, silica gel, alumina gel, activated carbon, synthetic aluminosilicates, and some other solids.

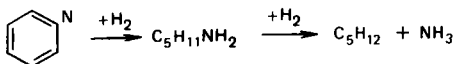
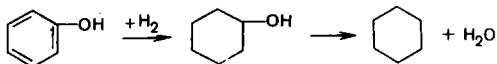
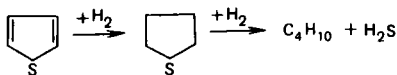
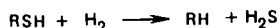
Catalytic processing is carried out to upgrade the products of crude oil fractionation and secondary refining processes. In industrial practice, catalysts are employed for removal of sulphur, nitrogen, oxygen and organometallic compounds over an Al-Co-Mo or Al-Ni-Mo catalyst in a hydrogen environment under pressure (collectively known as *hydrotreating*); removal of unsaturated hydrocarbons with the aid of synthetic aluminosilicates; removal of sulphur compounds with the aid of natural bauxites and aluminosilicates; and catalytic demercaptanization known as the Merox process which has gained popularity in and outside the Soviet Union in recent years. This process is effected over a special kind of catalyst in an alkaline environment:



The Merox catalyst is sensitive towards hydrogen sulphide, therefore the feed has first to be pre-treated with ethanol amine or an alkali.

Applications of hydrotreating are numerous, and the feedstocks thus processed include nearly all petroleum fuels, both straight-run and from secondary processes, namely: gasoline, kerosene, jet and Diesel fuels, and vacuum gas oil. Hydrotreating is also employed to upgrade lubricating oil components and paraffins.

The changes that sulphur, oxygen and nitrogen compounds undergo in hydrotreating may be illustrated by the following examples:



Hydrotreating is accompanied by the hydrogenation of unstable unsaturated hydrocarbons to the respective saturated compounds.

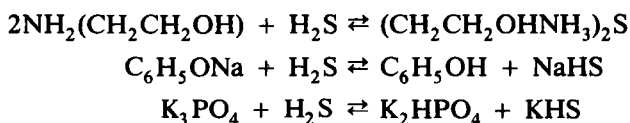
Treatment with selective solvents is most commonly used in the manufacture of lubricating oils. The selective solvents used on an industrial

scale are liquid sulphur dioxide, nitrobenzene, furfural, phenol, cresol, dichloroethane, urea, propylene carbonate, and some others.

With selective treatment, the solvent may take up the unwanted constituents without affecting or only slightly dissolving the principal components of the product, or it may dissolve the hydrocarbons while the impurities are precipitated from solution and can readily be separated.

All solvent extraction processes may be classed into single-pass, multiple-pass, batch, and countercurrent. The counter-current process is most effective because the product being processed is continuously moving against the stream of solvent.

Absorption is employed for removal of hydrogen sulphide. Most often, the absorbents used are ethanol amine, phenolates, and phosphates. In each case, the process is based on an applicable reversible reaction which proceeds according to the scheme:



Gases carrying carbon oxide and dioxide are treated for removal of hydrogen sulphide with arsenic and soda.

16.5 Environmental Pollution Abatement in Petroleum Refining

The total mass of petroleum hydrocarbons dumped into the World Ocean every year is estimated at 5-10 million tonnes. According to statistics, most of the pollution occurs when crude oil or petroleum products are in transit. For example, a good deal of crude oil is lost when the ocean-going supertankers carrying it are loaded, unloaded, cleaned, and ballasted.

Crude oil transportation is not the only source of ocean pollution. About the same contribution comes from the rivers and urban effluents.

A still greater quantity of petroleum hydrocarbons find their way into the atmosphere as a result of evaporation or incomplete fuel combustion. The processing and burning of low-quality petroleum is accompanied by the discharge to the atmosphere of hydrogen sulphide, mercaptanes, carbon monoxide, nitrogen oxides, and also the solid particles that form when the catalyst is regenerated in catalytic cracking processes. When petroleum products are upgraded, an amount of hydrocarbons leaks around valves, from pipelines, reactors, and storage tanks. A good deal of pollutants come with the wastewaters discharged to the sewers. The air is further polluted with the exhaust gases from automobiles, as they carry carbon monoxide, hydrocarbons, other organic compounds, nitrogen oxides, and sulphur-bearing compounds.

Quite naturally, every effort is made to minimize environmental pollution from petroleum refining. Current legislation requires that every 'grass-roots' petroleum refining complex should be equipped with facilities for removal of pollutants from the final effluents and emissions. Work never stops on improvements in these facilities, and better processes are being developed for the purpose, such as pressure flotation with the use of polyelectrolytes, and biochemical schemes which give water of a higher quality than can be taken from natural sources.

In recent years, the loss of petroleum and of its products in the USSR has been cut down by a factor of 1.3 owing to a package of measures such as proper sealing of tanks, venting devices, pump stations, and pipeline accessories, better handling of petroleum in transit and at oil terminals, and more efficient recovery of petroleum products from water-treatment facilities and from the purge gases from units to be shut down for repair.

Special promise with regard to environmental pollution abatement is held by processes leaving little or no wastes at all. Apart from that, they will make it possible to minimize water usage and to neutralize flue and waste gases.

An important problem facing the petroleum refining industry is the abatement of SO_2 emissions. At this writing, the level of SO_2 emissions per tonne of petroleum refined in the USSR is by a factor of 1.3-1.5 lower than it is outside the Soviet Union, but this is still considered inadequate. Therefore work is under way on novel processes for removal of SO_2 from the emissions of petroleum refining complexes. This, too, will moderate the detrimental effect on Nature.

Chapter Seventeen

CARBON MONOXIDE AND HYDROGEN BASED SYNTHESSES

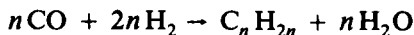
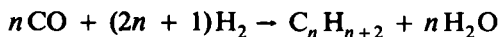
It is widely practised to synthesize organic compounds from carbon monoxide and hydrogen.

For the first time, catalytic synthesis of hydrocarbons from CO and H_2 was effected by P. Sabatier who synthesized CH_4 over a nickel catalyst, and by Orlov who produced ethylene over an iron-palladium catalyst applied to a coke base.

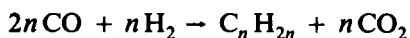
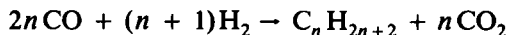
Thermodynamically, CO and H_2 can be synthesized into hydrocarbons of any molecular mass, type and structure. Currently, CO and H_2 are used to synthesize hydrocarbon mixtures of a broad fraction make-up (from C_1

to C_{30} and even, but more seldom, to C_{100} and higher), including alkanes and alkenes.

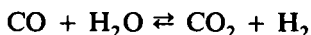
Generally, the synthesis of alkanes and alkenes from CO and H_2 over cobalt catalysts may be depicted as follows:



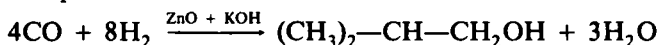
When this is done over an iron catalyst, the following reactions apply:



The formation of CO_2 over iron catalysts is due to the reaction



Fischer and Tropsch found that when the catalysts are oxides of some metals, the synthesis produces a mixture of hydrocarbons and oxygenated organic compounds, including methanol. The addition of an alkali to the oxide catalyst leads to the formation of higher alcohols among which isobutanol is predominant:



As is seen, the synthesis of hydrocarbons from carbon monoxide and hydrogen may follow any one of many routes, depending on the catalysts used and the operating conditions adopted. Synthesis over a nickel catalyst at a pressure of 0.1 MPa and a temperature of 160-200 °C yields alkanes and alkenes with more than 2 carbon atoms per molecule, while at a temperature of over 200 °C the product is mainly methane. When the synthesis is effected over a cobalt catalyst at a pressure of 0.1-1 MPa and a temperature of 170-200 °C, the products are alkanes and alkenes, predominantly of straight-chain structure. When use is made of iron catalysts at a pressure of 2-3 MPa and a temperature of 200-250 °C, the synthesis produces mixtures of alkanes and alkenes, primarily of branched structure, and also oxygenated organic compounds. Synthesis over ruthenium catalysts at high pressure (50-150 MPa) and high temperature (100-120 °C) yields high-molecular-weight paraffins (with a molecular mass of 2×10^5 and more).

The thermodynamic feasibility and experimental scope of synthesis of various oxygenated organic compounds from CO and H_2 are enhanced through the use of $CO + H_2O$, $CO_2 + H_2$ and $C_3O_2 + H_2$ mixtures, the addition of initiators, active and complex-forming solvents, and the use of high pressure (up to 1000 MPa).

For the first time the Fischer-Tropsch process was implemented in Germany in 1936 for the production of synthetic gasoline, called synthine.

Currently, mixtures of carbon monoxide and hydrogen are used for the industrial tonnage production of methanol, liquid aliphatic hydrocarbons, and methane. Their world production is estimated at 25 million t/yr.

17.1 Methanol Synthesis

In significance and scope of production, methanol at present is among the most important tonnage products turned out by the chemical process industries. Methanol is a key material in the manufacture of plastics, synthetic fibres, synthetic rubber, as a solvent, etc.

The field of application for methanol is expanding all the time. Notably, it holds special promise as the working medium for the transport of energy over long distances, a likely component of automotive gasoline, a raw material for microbiological synthesis, etc.

For the first time the production of methanol by its synthesis from carbon monoxide and hydrogen was commercialized in Germany in 1923, and in 1978 its world production exceeded 10 million t/yr. It is a safe guess that in 1980s its production will be 90 million t/yr.

The growth of the world's production of methanol in recent decades is illustrated in Table 17.1 which lists its major producers outside the USSR. As is seen, methanol production doubled every decade.

The feed gas for methanol production is synthesis gas. It can be produced from several fuel sources. As the matters stand in this respect in the USSR can be seen from the data listed below.

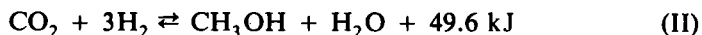
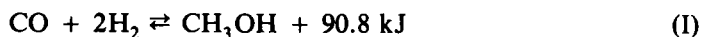
Natural gas	71.6
Acetylene synthesis gas	15.7
Petroleum refinery gases	3.8
Solid fuels	8.9

Table 17.1 Methanol Production by Leading Producers
(thou. t/yr)

Country	1960	1965	1970	1975	1980
USA	892	1300	2242	2250	4000
Japan	193	430	938	1360	2000
West Germany	333	603	863	1200	1600
Italy	112	150	284	300	400
France	70	123	212	400	530
Great Britain	57	160	212	340	400

Coal gasification for the production of synthesis gas carrying H_2 , CO_2 and CO may change the pattern of raw material supplies for methanol synthesis. In this way, hard-to-carry coal will be converted to methanol convenient to store, ship, and use.

Physico-chemical foundations of methanol synthesis. Methanol synthesis is based on the following reversible reactions:



Reactions (I) and (II) are exothermic and proceed with a reduction in volume. It follows then that in order to achieve a maximum yield of methanol and a maximum conversion of synthesis gas, the process must be effected at a low temperature and a high pressure.

The maximum achievable conversion of synthesis gas is limited by the equilibrium conditions of methanol synthesis. These conditions have been explored both theoretically and experimentally. The following equation has been derived for the equilibrium constant of Reaction (I):

$$\log_{10} K_p = 3748.7/T - 9.2833 \log_{10} T + 3.1475 \times 10^{-3} T - 4.2613 \times 10^{-7} T^2 + 13.8144$$

The equilibrium constant of Reaction (II) can be found from the equilibrium constant of Reaction (I), and also from the equilibrium constant of the reaction accompanying the formation of methanol:

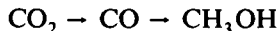


Here,

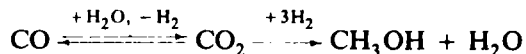
$$K_2 = K_1/K_3$$

The above procedure is applicable to our case because Reaction (II) can be deduced on subtracting Reaction (III) from Reaction (I) (see Chap. 2).

It is relevant to note that formerly the production of methanol from carbon oxides was visualized as a consecutive reduction of the carbon dioxide to carbon monoxide, and then of the carbon monoxide to methanol:



A research team at the USSR Academy of Science's Institute of Petrochemical Synthesis has proved that a new mechanism applies to methanol synthesis from carbon oxides. By this mechanism, methanol is formed over copper-zinc-aluminium or zinc-chromium oxide catalysts from the carbon dioxide that is present in the feed gas or is formed as the carbon monoxide is reformed by steam. Methanol synthesis from CO and H_2 proceeds according to the scheme



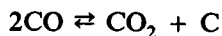
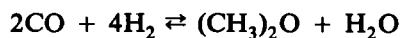
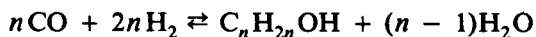
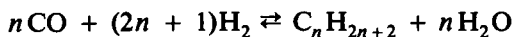
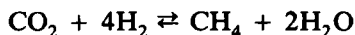
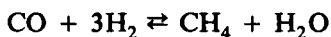
It follows then that "direct" methanol synthesis from CO_2 and H_2 is the principal route.

Table 17.2 lists the equilibrium concentrations of methanol calculated for a 2:1 hydrogen/carbon monoxide feedstock.

Table 17.2 Equilibrium Concentrations of Methanol in a 2:1 Hydrogen/Carbon Monoxide Feedstock

Pressure, MPa	Methanol concentration, vol.%, at temperature, °C	
	300	350
5	10.5	—
7.5	—	4.9
10.0	26.3	8.2
15.0	40.8	16.0
20.0	54.0	24.0
25.0	66.0	31.9
30.0	75.5	40.4
40.0	86.0	55.5
50.0	89.6	66.7

It is seen from Table 17.2 that the methanol content of the stock increases with increasing pressure and decreasing temperature. It is necessary, however, to raise the temperature if the reaction is to proceed at a high rate. Also, when choosing an optimum operating temperature, account must be taken of the side reactions that produce methane, higher alcohols, acids, aldehydes, ketones and others:



These reactions are responsible for the wastage of some synthesis gas and add to the cost of methanol refining.

The catalysts used in methanol synthesis must be very selective towards the methanol reaction, that is, give a reaction rate for methanol much

faster than that of the competing reactions. Many catalysts have been proposed for the purpose.

Early tonnage units effected methanol synthesis at a pressure of around 30 MPa and a temperature of 300-400 °C over a zinc-chromium catalyst. Later, processes effected at lower pressures and using low-temperature catalysts came to the fore. The current practice is to effect the process at a pressure of 50-60 MPa and a temperature of 250-260 °C over a catalyst which is a mixture of zinc, chromium and copper oxides.

Methanol synthesis catalysts are highly sensitive towards catalyst poisons. Therefore, the first step in the process is the desulphurization of the feedstock. Sulphur compounds poison the zinc-chromium catalysts reversibly (temporary poisoning), and the copper catalysts irreversibly (permanent poisoning). A further requirement is a thorough removal of the iron carbonyl which is formed as a result of the reaction between the carbon monoxide of the feed and the iron of the equipment. Depositing on the catalyst, the iron carbonyl decomposes with the evolution of elemental iron, and this favours the formation of methane.

In building a mathematical model for the process, one needs equations relating the rate of reaction to the process variables. Quite a number of works have been devoted to the kinetics of methanol synthesis. On their basis the rate of reaction over a zinc-chromium catalyst (with the reaction proceeding in an ebullated bed and with the rate controlled by the adsorption of hydrogen) may be written thus

$$w = k_1(p_{\text{H}_2}p_{\text{CO}}^{0.5}/p_{\text{CH}_3\text{OH}}^{0.25}) - k_2(p_{\text{CH}_3\text{OH}}^{0.25}/p_{\text{CO}}^{0.25}) \quad (17.2)$$

where:

- k_1 = rate constant of the forward reaction
- k_2 = rate constant of the backward reaction
- p = partial pressure

The rate of reaction over a copper-zinc-aluminium catalyst can be found by the following equation

$$w = k_1(p_{\text{CO}}^{0.5}p_{\text{H}_2}/p_{\text{CH}_3\text{OH}}^{0.66} - p_{\text{CH}_3\text{OH}}^{0.34}/p_{\text{CO}}^{0.5}p_{\text{H}_2}K) \quad (17.3)$$

where:

- k_1 = rate constant of the forward reaction
- K = equilibrium constant

The rate constant k_1 in Eq. (17.3) may be found by the following formula:

$$k_1 = 7.734 \times 10^8 \exp(-22\,700/RT) \quad (17.4)$$

A plot relating methanol yield to temperature appears in Fig. 17.1. The

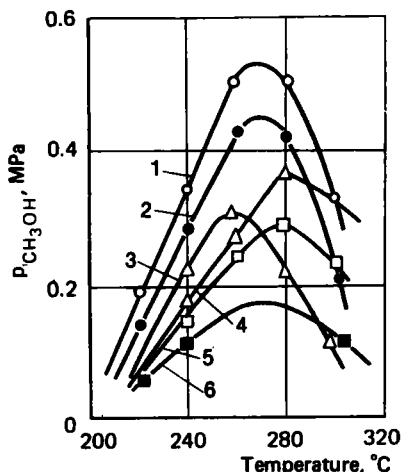


Fig. 17.1 Methanol yield as a function of temperature at CO partial pressures of 1.08, 0.47 and 2.0 MPa. Contact time: 1, 2, 3 — 0.29 s; 4, 5 — 0.10 s

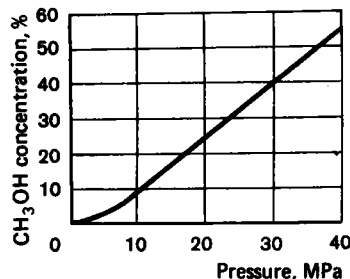


Fig. 17.2 Methanol yield as a function of pressure at a temperature of 350 °C and a 2:1 H₂/CO ratio

curves have peaks with any composition of the feed, and the methanol yield is maximum at 255-270 °C.

The optimum temperature range conducive to the highest product yield is decided by catalyst activity, the volumetric flow rate of the feed, and pressure.

The effect of pressure on methanol synthesis is illustrated in Fig. 17.2. The low-pressure processes (5-10 MPa) over copper-bearing catalysts are effected in the temperature range of 220-280 °C. Zinc-chromium catalysts are typically associated with processes effected at higher pressures (20-30 MPa) and higher temperatures (350-400 °C). In industrial practice, the pressure limit is set at 40 MPa. Higher pressure would favour the side reactions and would add to the cost of synthesis gas compression, thereby impairing the economy of methanol synthesis operations. In the low-pressure methanol synthesis processes, the pressure limit is set by the thermal stability of copper catalysts.

Methanol yield falls off with increasing volumetric flow rate. This applies to both high-pressure and low-pressure synthesis. The reason is that an increase in the volumetric flow rate of the feed cuts down the time during which the feed is in contact with the catalyst and, in consequence, reduces the methanol content of the gas leaving the reactor (see Fig. 17.1).

A plot of catalyst capacity as a function of volumetric flow rate at 30 MPa is shown in Fig. 17.3. As the feed flow increases (and the contact time decreases), the methanol content of the gas decreases. However, the

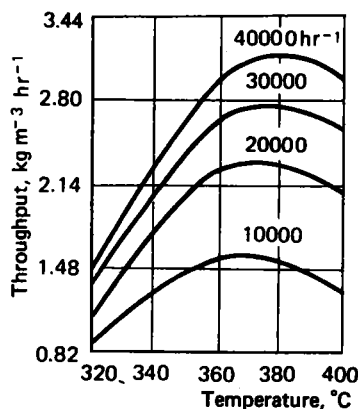


Fig. 17.3 Catalyst capacity at 30 MPa as a function of volumetric flow rate

catalyst capacity increases because a greater volume of gas passes per unit time through the same volume of catalyst. In practice, methanol synthesis is effected at a volumetric flow rate of 20 000-40 000 hr⁻¹.

The conversion of synthesis gas per pass through the reactor is limited by the equilibrium position in the formation of CH₃OH from CO and H₂, and the maximum allowable temperature drop across the catalyst bed when the process is effected adiabatically. The conversion of CO per pass is 15-50%, with the result that the contact gases carry just about 4% methanol. One way to enhance the conversion of the synthesis gas is to recycle it upon the separation of the methanol and water. The recycle ratio can be found on the basis of the relation that exists between the conversion of CO per pass and the desired overall conversion:

$$x_{\text{CO}} = x'_{\text{CO}} \frac{1 + m}{1 + m(1 - C_A/C_0)} \quad (17.5)$$

where:

- x_{CO} = overall conversion of CO
- x'_{CO} = CO conversion per pass
- m = recycle ratio
- C_0 = CO concentration in the inlet feed
- C_A = CO concentration in the gas leaving the condensation step

With recycling, the inert impurities methane, nitrogen and argon build up in the synthesis gas, and their concentration has to be controlled by purging.

An increase in the concentration of the inert constituents in the feed gas is equivalent to a decrease in the partial pressure of the reactants, and this brings down the capacity of the catalyst. The composition of the feed gas has a vital bearing on its conversion and catalyst capacity. In industrial

practice, it is customary to operate with an excess of hydrogen. The maximum throughput is obtained with a 4:1 hydrogen / carbon monoxide feed. In practice, use is made of a 2.15:1 to 2.25:1 ratio.

Methanol production schemes. The production of methanol from CO and H_2 comprises a number of operations which are essential in any process configuration. To begin with, iron carbonyl and sulphur compounds are removed from the reformer feed which is then preheated to the kindling temperature of the reaction and is passed to a methanol synthesis reactor. As the gas leaves the catalyst zone, its methanol is separated by cooling the mixture which is then compressed to the synthesis pressure and recycled. A block diagram of methanol synthesis is shown in Fig. 17.4.

Various plants mainly differ in the items employed at the synthesis step — the synthesis reactor and the heat exchanger. Figure 17.5 shows a flowsheet for the high-pressure process of methanol manufacture, incorporating an integrated packing. Compressed to 32 MPa, the synthesis gas is purified in an oil filter, 1, and a carbon filter, 2, following which it is mixed with the recycled gas. The mixture passes through the annular clearance between the catalyst box and the shell of the reactor, 3, and

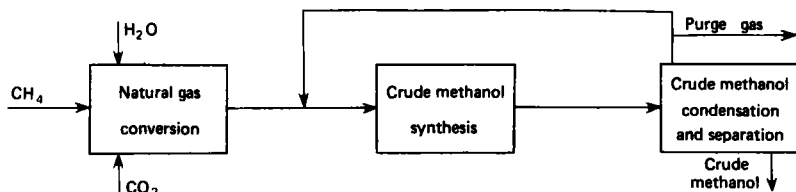


Fig. 17.4 Block diagram of methanol synthesis

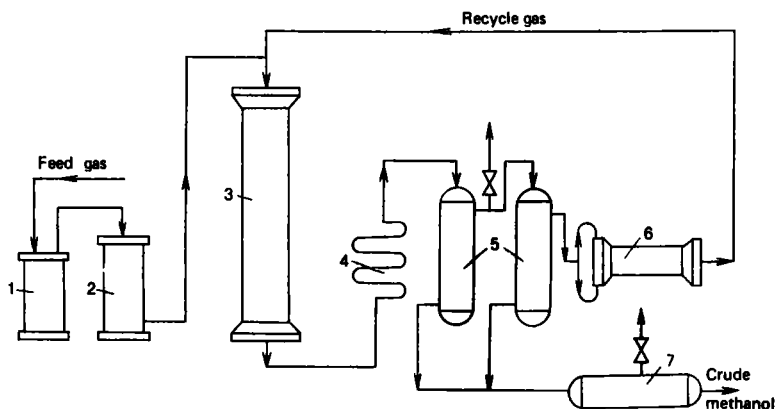


Fig. 17.5 Flowsheet of an integrated-packing methanol synthesis unit:

1, oil filter; 2, carbon filter; 3, reactor; 4, cooler-condenser; 5, separators; 6, compressor; 7, collector

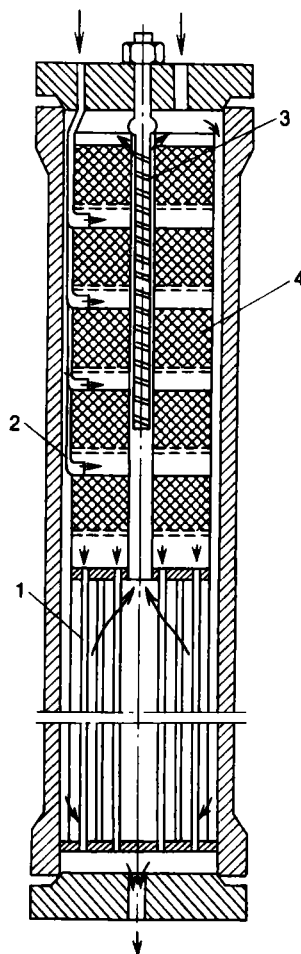


Fig. 17.6 Methanol reactor:

1, heat exchanger; 2, cold bypass; 3, electric preheater;
4, catalyst

enters the tube side of the heat exchanger located at the base of the reactor (Fig. 17.6). In the heat exchanger, the gas is heated to 330-340 °C and conveyed over the central pipe enclosing an electric heater to the top of the reactor. As the gas stream descends, it consecutively passes through the five catalyst beds. Following each catalyst bed, except the last one, a certain amount of cold recycled gas is added in order to maintain the temperature at a constant value. On passing through the 5th catalyst bed, the gas is routed to a heat exchanger where it is cooled from 300-385 °C to 130 °C, and then to a cooler-condenser of the double-pipe type, 4 (see Fig. 17.5). Here the gas is cooled to 30-35 °C, and the synthesis products are condensed. The raw methanol is separated in a separator, 5, passed to a

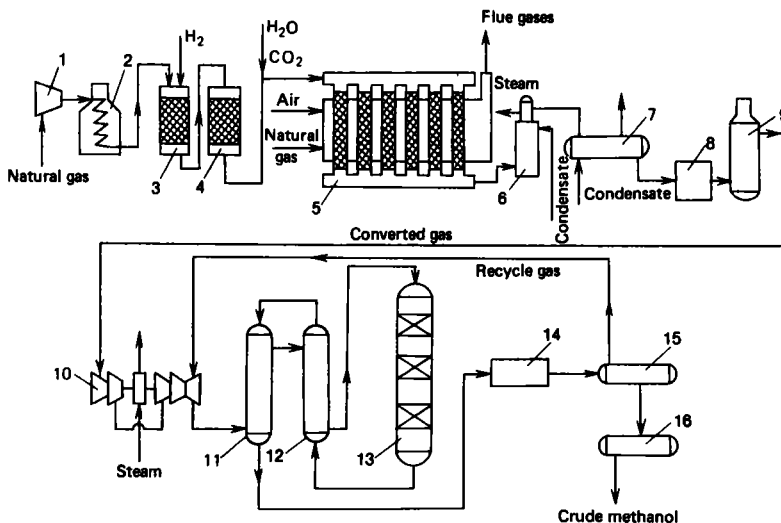


Fig. 17.7 Flowsheet for the manufacture of methanol at a pressure of 5 MPa:

1, turbocompressor; 2, natural gas preheater; 3, desulphurizer; 4, adsorber; 5, reformer; 6, waste-heat boiler; 7, heat exchanger; 8, cooler-condenser; 9, separator; 10, turbocompressor; 11, 12, heat exchangers; 13, methanol reactor; 14, cooler-condenser; 15, separator; 16, collector

collector, 7, and withdrawn for rectification. The gas is passed through a second separator, 5, for removal of methanol droplets, compressed to the synthesis pressure by a circulating turbocompressor, 6, and recycled to the synthesis step. The purge gases are withdrawn ahead of the compressor and burned as fuel along with the tank gases.

Since the heat exchanger is located inside the reactor shell, appreciably less heat is lost to the surroundings. This improves the conditions for the autothermal operation of the unit and makes unnecessary any hot pipelines, thus enhancing the safety of operation and cutting down the overall capital costs. Also, the shorter pipelines present a lower hydraulic resistance in the system so that circulating turbocompressors may be used instead of the reciprocating type.

The low-pressure methanol synthesis process includes practically the same steps, but also has some differences. The flowsheet of a 300 thousand t/yr methanol synthesis unit operating at a pressure of 5 MPa and using natural gas as the reformer feedstock is shown in Fig. 17.7.

Referring to the diagram, the natural gas feedstock is compressed by a turbocompressor, 1, to a pressure of 3 MPa, preheated in a preheater, 2, by the combustion gases obtained by burning natural gas on the tube side, and passed to a desulphurizer, 3 and an adsorber, 4, where the organic sulphur compounds are catalytically hydrogenated, and the hydrogen

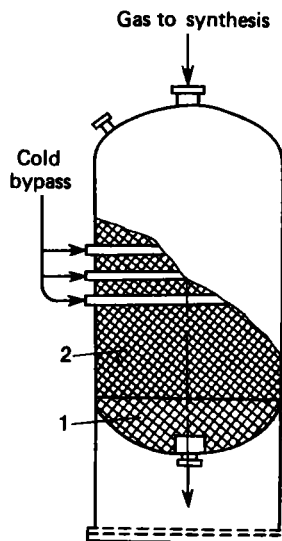


Fig. 17.8 Low-pressure methanol reactor:
1, porcelain balls; 2, catalyst

sulphide thus formed is taken up by a zinc-oxide based adsorbent. Following that, the feed gas is mixed with steam and carbon dioxide in a 1:3.3:0.24 $\text{CH}_4/\text{H}_2\text{O}/\text{CO}_2$ ratio. The mixture is passed to a tubular reformer, 5, where the steam-carbon dioxide mixture is reformed over a nickel catalyst at a temperature of 850-870 °C. The heat required for the reforming step is obtained by burning natural gas in suitably designed burners. The reformed gas then goes to a heat exchanger, 7, to preheat the feedwater for the waste-heat boiler. On passing through a cooler, 8, and a separator, 9, the gas is cooled to 35-40 °C. The cooled reformed gas is compressed to a pressure of 5 MPa in a compressor, 10, mixed with the recycle, and passed to heat exchangers, 11 and 12, where it is heated to 220-230 °C. The hot gas mixture enters a synthesis reactor, 13, where the temperature is controlled with the aid of cold by-passes. The heat of reaction is reclaimed by heat exchangers 11 and 12 to heat the gas entering the reactor. The gas mixture is then cooled in a cooler-condenser, 14, the condensed raw methanol is separated in a separator, 15, and passed to a collector, 16. The recycled gas goes to the reactor, while the purge and tank gases are burned in a tube furnace.

Owing to the decrease in temperature, the low-pressure methanol synthesis process takes place under conditions very close to equilibrium, and this enhances the throughput of the synthesis unit.

A reactor for low-pressure methanol synthesis is shown in Fig. 17.8.

Low-pressure methanol synthesis reactors are simpler to design and fabricate because the process goes on under milder conditions. The reactors may be of both the shaft type and the tubular type. A matter of special

concern with regard to low-pressure synthesis reactors is withdrawal of heat because copper-bearing catalysts are more sensitive towards temperature variations than zinc-chromium catalysts. In shaft reactors, the temperature is controlled with the aid of bypasses in which case the cold gas is introduced via suitably designed manifolds. In tubular reactors the catalyst is enclosed in tubes cooled by boiling water. The catalyst temperature is maintained at a constant value over the entire length of the reactor with the aid of pressure controllers so that the overheating of the catalyst is practically avoided. The spent catalyst is as simple to discharge upon removal of the bar screens. The reactor diameter is up to 6 m with a length of 8-16 m.

17.2 Recent Trends in Methanol Manufacture

In last years, methanol has markedly expanded its field of application. There has been a continuous increase in the number of products for which methanol is a key feedstock. Among them are formalin, urea resins, acetic acid, synthetic rubber, pesticides, polyvinyl alcohol, acetal, anti-freeze compounds, and denaturants, to name only a few. There has been growing interest in methanol as the starting material for the manufacture of hydrogen and synthesis gas widely used in metal-making, ammonia synthesis, and desulphurization of petroleum products. Progressively larger quantities of methanol are being used in the manufacture of acetic acid, denitrification of sewage waters, and the preparation of feed-grade proteins. It is envisaged that methanol will shortly find use as a source of energy, as a fuel gas for thermal power stations, as a motor fuel, and as a component of automotive gasoline. When doped with methanol, gasoline acquires a better antiknock quality, the engine efficiency is enhanced, and the exhaust gases contain far less objectionable pollutants.

The expanding field of application for methanol calls for more effort to be put into the improvement of its production. One way is to use plants of ever larger unit capacity, processing of synthesis gas without a reforming step, merger of methanol synthesis with other nitrogen product processes, and use of centrifugal compressors. The reliability of centrifugal compressors which are the most sophisticated and critical pieces of process plant is at the same time an indicator of how reliable the entire synthesis unit is and how consistent it is in performance.

17.3 Environmental Pollution Abatement in Methanol Manufacture

The gas emissions from methanol production may be permanent and intermittent. The permanent emissions include the off-gases and fumes evolved from the raw methanol at the distillation step, and also the purge

gases from the various vessels. The intermittent emissions which are the principal contributors of air pollution occur at the time of shut-down which may involve a whole plant, a plant unit, a plant item, or other pieces of equipment. When a shut-down item is purged, the remaining gases and vapours are discharged to the atmosphere. It is therefore clear that air pollution with gas emissions can best be abated by enhancing the reliability of all plant items and units so as to minimize the number and duration of shut-downs and start-ups and to extend the time to repair.

Another major source of pollutants from methanol manufacture is wastewater. It contains as much as 0.3% methanol and other oxygenated organic compounds. The most important among the total wastewater are sludge and tank wash waters and the wastes from the methanol purification step. A nearly complete purification of wastewaters can be achieved only by biological processing in activated-sludge aeration tanks. The limit of the methanol concentration in the wastewaters coming in for biological processing is set at 200 mg l^{-1} . As a rule, before they enter the biological processing step, wastewaters from methanol synthesis are repeatedly diluted with wastewaters from other processes and with sewage water.

Chapter Eighteen

AN OUTLINE OF BIOENGINEERING

Bioengineering, or biotechnology, is an up-coming and rapidly expanding division of the high-technology field. As it stands today, bioengineering encompasses microbiological synthesis, genetic engineering, fermentation technology, tissue culturing, cell hybridization, and some other fields.

18.1 Microbiological Synthesis

Microbiological synthesis is based on microbial activity which brings about complex biochemical conversions to yield a desired biomass or the products of its life processes.

The reactions involved here take place in and outside the cells of microorganisms — bacteria and yeasts — under the influence of the enzymes secreted by these microorganisms. Commercial processes use microorganisms capable of reproduction at a very high rate (to date, bacteria and yeasts have been isolated that can build up their biomass 500 times faster than do the most high-yield crops) and also of oversynthesis (that is, the formation of metabolites, such as amino acids, vitamins, nucleotides, etc. in excess of what is needed to sustain the microbial cell).

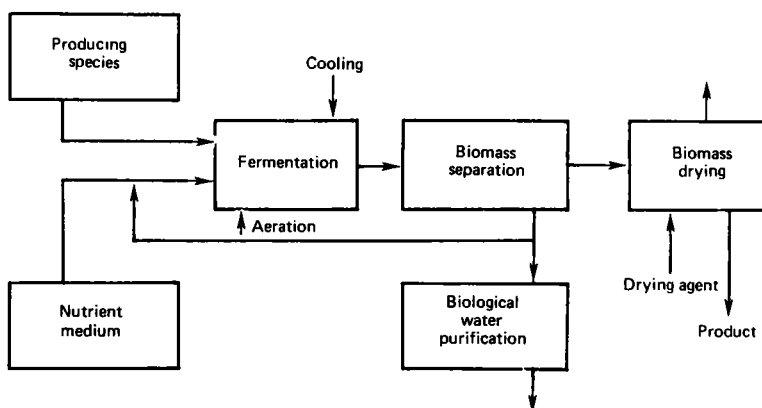


Fig. 18.1 Production of biomass

Such microorganisms can be isolated from natural sources or grown artificially, using the techniques of genetic engineering or other methods.

A microbiological synthesis process (Fig. 18.1) involves the following basic steps.

(1) A highly productive culture of a microorganism (the producing species) is prepared.

(2) A suitable feed, called the substrate, is prepared to sustain the producing species.

(3) The producing species is grown.

(4) The producing species is cultivated under specified conditions so that the desired microbial reactions take place. This is the fermentation step.

(5) The biomass is thickened and separated or the desired end product is extracted and purified. This step is effected in separators, flotators, filters, and evaporators.

(6) The thickened biomass is dried.

(7) The finished product is obtained.

Some of the broth drawn off at the biomass thickening step is recycled to the fermenter, while the remainder is subjected to biological processing and withdrawn from the process.

The growth and development of the microorganisms selected for synthesis purposes are governed by a large number of factors related to the environment. The most important among them are the substrate, oxygen uptake, temperature, pressure, pH value, and redox potential.

The substrate consists of organic and inorganic compounds. The carbon required for the growth of the microorganisms can be obtained from various hydrocarbons, such as *n*-paraffins, methane, and gas oil. The best source of carbon are carbohydrates. The current industrial practice gives

preference to the derivation of proteins from purified liquid paraffins. In the future it is planned to use methanol on a large scale for the purpose. Protein biosynthesis from methanol is relatively easy to effect and does not call for heavy energy expenditures.

The essential inorganic components of the substrate are nitrogen, phosphorus, magnesium, potassium, iron, zinc, and manganese. The substrate also includes the trace amounts of the elements molybdenum, copper, cobalt, calcium, nickel, sulphur, chlorine, sodium, and some others. The deficiency in any of these inorganic elements might cause heavy damage to the development and composition of the cells.

The required concentration of inorganic elements in the substrate can be found from the balances on the nutrients in the process and their uptake by the microorganisms:

$$C^i = C_0^i - \alpha^i \mu x (V/v)$$

where:

- C_0^i = initial concentration of the nutrient, kg m^{-3}
- C^i = final concentration of the same nutrient, kg m^{-3}
- α^i = specific consumption of the nutrient, kg kg^{-1}
- μ = growth rate of the microorganisms, hr^{-1}
- x = cell concentration, kg m^{-3}
- V = fermenter volume, m^3
- v = volumetric flow rate, $\text{m}^3 \text{hr}^{-1}$

The productivity of microbiological synthesis is markedly affected by oxygen. Oxygen takes part in the respiration of aerobic microorganisms as the electron acceptor in the respiratory circuit of the cell. It is also a part of the substrate that makes up the cell mass.

The specific oxygen demand, in kg O_2 per kg of biomass, may be defined as

$$\alpha^{\text{O}_2} = a + b/\mu$$

where:

- a = coefficient taking care of the oxygen demand to sustain the growth, $\text{kg O}_2 \text{kg}^{-1}$ of biomass
- b = coefficient taking care of the oxygen required to sustain life processes, $\text{kg kg}^{-1} \text{hr}^{-1}$
- μ = specific growth rate of microorganisms, hr^{-1}

Taking the growth of yeasts on a carbon substrate as an example, the above relation within the feasible range of growth rates has the form

$$\alpha^{\text{O}_2} = 1.35 + 0.125/\mu$$

Temperature affects both the growth of the biomass and the cell make-up. For carbon-oxidizing yeasts, the optimum temperature range is

305-307K. Most methane-oxidizing bacteria have a temperature of 303K. Biosynthesis evolves a large quantity of heat which has to be removed.

Pressures up to 1.01×10^6 Pa affect but little the metabolism of cells. A pressure of 1.01×10^7 Pa and higher inhibits the growth and propagation of most microorganisms.

The pH value of the substrate affects the activity, growth, and propagation of microorganisms in a fairly complicated manner. For some microorganisms, the optimum pH value range is from 4 to 9. The best choice for yeasts, for example, is a pH value of 4 to 6.

It has been found that the redox potential has a well defined effect on the specific growth rate of yeasts.

For analysis and design purposes, it is assumed that the products of biosynthesis are only biomass, water, and carbon dioxide.

The principal step of microbiological synthesis is the biochemical conversion effected in a biochemical reactor called the fermenter or fermentator. Fermenters may be continuous or cyclic, sterile (hermetically sealed) or non-sterile. The mechanical design of a fermenter depends on the substratum to be used, which may be liquids (such as paraffins, distillates, and hydrolysates) or gases (such as methane or carbon dioxide), and also on the quantity of oxygen required to sustain the process, and the thermal effect of the biosynthesis reaction. Among the key requirements to be met by a fermenter are provision for high-rate mass and heat transfer, high level of homogenization, and turbulence in the reactor.

Microbiological technology as it stands in the USSR at this writing mainly produces crop-stimulating agents, animal-feed supplements, including feed-grade yeasts and the essential amino acids (notably lysine), premixes, vitamins, enzymes, feed-grade and veterinary antibiotics, microbiological pesticides and disinfectants, bacterial fertilizers, etc. There is a continuous expansion in the production of agents for the textile, food-processing, pharmaceutical, chemical and other industries and for research. Special promise is held by microbiological agents for the processing of hides, pelts and furs, the manufacture of perfumes and cosmetics, flax processing, detergent manufacture, and some other fields.

18.2 Genetic Engineering

Genetic engineering is essentially the art and science of 'cutting and stitching' deoxyribonucleic acid (DNA) into what is known as *recombinant DNA* or *rDNA*, carrying the desired genetic information. It is one of the most promising divisions of bioengineering as it offers a means of introducing into a bacterial host cell the genetic code, or genes, from practically any organism, including the human being, thus converting it into a highly efficient protein factory for medicine, agriculture, and industry.

When suitable foreign genes are 'stitched' into the cells of bacteria, these cells will then manufacture human proteins, such as interferon, insulin, growth hormones and other valuable drugs and diagnostic reagents. It also offers a means for the improvement and/or development of highly efficient bacterial strains for the manufacture of antibiotics, amino acids, vitamins, and new microbial cultures that can in turn be utilized in the chemical process and food industries and as energy sources.

Genetic engineering has proved a success in plant breeding. By introducing new genes into plant cells, it is possible to endow plants with qualities that will enhance their resistance to environmental factors and step up photosynthesis rate, and with the ability to fix molecular nitrogen from the air into usable forms by themselves or to establish symbiotic relationships with nitrogen-fixing bacteria thriving on plant roots. By imparting high-rate photosynthesis and nitrogen-fixing abilities, wheat, rice and other cereal crops can be converted into varieties of an extremely high protein content without having to put in more fertilizers. As a corollary, this will also save energy, notably gas and petroleum which are used as feedstocks in the manufacture of nitrogen fertilizers.

18.3 Fermentation Technology

Fermentation technology, or the use of enzymes as biocatalysts in the industrial production of a wide gamut of substances, is a highly promising division of bioengineering. Enzymes increase the rate of reaction millions of times. As they do so, they also allow a substantial reduction in the temperature and pressure used in chemical processes, thus making them less energy-intensive and independent of expensive inorganic catalysts. Importantly, fermentation synthesis of polymers does not pollute the atmosphere in which respect it compares favourably with the chemical synthesis of these materials.

In some cases, enzymes are immobilized, or trapped, in a suitable substrate — this makes them more convenient to handle and to use repeatedly.

Among other things, fermentation technology is to be used for the preparation of prostaglandins, biologically active substances of high value to medicine, livestock breeding, and veterinary science. Work is under way on a fermentation process for the production of glucose from the cellulose of cotton lint. When commercialized, this process will help to expand the production of this valuable product many times and to obtain a high economic benefit.

The fermentation hydrolysis of straw, corn stalks and cobs, cotton stalks, wood chips and other cellulose-rich wastes, followed by microbial yeast synthesis, will fill the gap existing in the supply of feed-grade yeasts.

18.4 Future Prospects

Bioengineering is rapidly expanding to encompass many other fields, such as mining, metal making, chemicals, and light industries. An impressive headway has been made in biogeotechnology. A wealth of experience has been accumulated in the use of microorganisms for the recovery of non-ferrous metals, uranium and gold by their bacterial leaching out of lean or hard-to-dress ores.

The USSR and some other countries have advanced in the bacterial-chemical leaching of complex copper, zinc, nickel, copper-zinc, tin- and gold-bearing arsenic concentrates for further processing. Apart from being attractive ecologically, these processes render economically justified the treatment of lean ores, wastes, marginal and deep-lying orebodies and provide for a more complete recovery of all values from mineral raw materials.

Bacteria may be used to bring down the methane content of the air in collieries. The bacteria used for the purpose are highly active in oxidizing methane to carbon dioxide and able to thrive on very simple, inorganic nutrients. Many experiments have shown that in a matter of 2 to 4 weeks such bacteria can oxidize as much as 60-70% of the methane present in the mine's atmosphere. This greatly minimizes the explosion hazard and enables coal winning operations to be stepped up appreciably.

Microorganisms and their metabolites may also be used to enhance petroleum recovery from 'difficult' horizons. Measures are being taken to set up the manufacture of biopolymers which will ease the drilling of oil and gas wells.

Bioengineering can do much to improve land usage and management. Among other things, agents are being developed to help recultivate land at sites of mining operations.

Research is in progress on the production of bacterial biomass for the biodegradation of toxic compounds, such as phenol and its derivatives, herbicides, pesticides, and xenobiotines, and for the treatment of wastewaters from the food, chemical, metal-making, petrochemical, and petroleum processing industries. Bioengineering is taking on an ever more important role in solving the problem of energy supply.

When used on a large scale, bioengineering will be contributing more and more to tackling the global problems of our time — the supply of food, raw materials and energy and the protection of the environment.

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